

National Library of Canada

Bibliothèque nationale du Canada

Direction des acquisitions et

des services bibliographiques

Acquisitions and Bibliographic Services Branch

395 Wellington Street Ottawa, Ontario K1A 0N4 395, rue Wellington Ottawa (Ontario) K1A 0N4

Your file Votre référence

Our tile Notre référence

### NOTICE

AVIS

The quality of this microform is heavily dependent upon the quality of the original thes.s submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter rithbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments. La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

2

Canada

Star Strange

## CONTROL OF A POLYPROPYLENE VISBREAKING PROCESS USING AN IN-LINE PROCESS RHEOMETER

by Burke I. Nelson

A Thesis Submitted to the Faculty of Graduate Studies and Research in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

> Department of Chemical Engineering McGill University, Montreal, Canada July, 1994

> > <sup>©</sup> Burke Irving Nelson, 1994



National Library of Canada

Acquisitions and Bibliographic Services Branch

395 Wellington Street Ottawa, Ontario K1A 0N4 Bibliothèque nationale du Canada

Direction des acquisitions et des services bibliographiques

395, rue Wellington Ottawa (Ontario) K1A 0N4

Your file Votre rélérence

Our file Notre référence

THE AUTHOR HAS GRANTED AN IRREVOCABLE NON-EXCLUSIVE LICENCE ALLOWING THE NATIONAL LIBRARY OF CANADA TO REPRODUCE, LOAN, DISTRIBUTE OR SELL COPIES OF HIS/HER THESIS BY ANY MEANS AND IN ANY FORM OR FORMAT, MAKING THIS THESIS AVAILABLE TO INTERESTED PERSONS. L'AUTEUR A ACCORDE UNE LICENCE IRREVOCABLE ET NON EXCLUSIVE PERMETTANT A LA BIBLIOTHEQUE NATIONALE DU CANADA DE REPRODUIRE, PRETER, DISTRIBUER OU VENDRE DES COPIES DE SA THESE DE QUELQUE MANIERE ET SOUS QUELQUE FORME QUE CE SOIT POUR METTRE DES EXEMPLAIRES DE CETTE THESE A LA DISPOSITION DES PERSONNE INTERESSEES.

THE AUTHOR RETAINS OWNERSHIP OF THE COPYRIGHT IN HIS/HER THESIS. NEITHER THE THESIS NOR SUBSTANTIAL EXTRACTS FROM IT MAY BE PRINTED OR OTHERWISE REPRODUCED WITHOUT HIS/HER PERMISSION. L'AUTEUR CONSERVE LA PROPRIETE DU DROIT D'AUTEUR QUI PROTEGE SA THESE. NI LA THESE NI DES EXTRAITS SUBSTANTIELS DE CELLE-CI NE DOIVENT ETRE IMPRIMES OU AUTREMENT REPRODUITS SANS SON AUTORISATION.

ISBN 0-612-00117-2

# **Canadä**

### CONTROL OF POLYPROPYLENE VISBREAKING USING AN IN-LINE RHEOMETER

.

.

#### Abstract

An in-line process rheometer, employing a proven shear-stress transducer, was designed and built for polymer melts. The entire process stream runs through the rheometer, giving it a much faster response time than conventional side-stream models. The possibility of using the in-line rheometer for dynamic mechanical analysis was investigated and methods were developed to obtain the complex modulus over a wide range of frequencies with a single measurement. Measurement techniques for shear viscosity testing were also developed along with algorithms to compensate for the effects of process pressure and temperature.

The rheometer was used as a viscosity sensor to provide feedback control for a polypropylene visbreaking process. A first order plus dead time model was used to model the process and the rheometer together, and typically had dead times of less than 60 s and a first order time constant of 15 s. Gain scheduling was incorporated into minimum variance and proportional-integral controllers to achieve closed-loop settling times of 200 s for viscosity setpoint changes and process disturbances.

<u>Résumé</u>

Un rhéomètre en ligne employant un capteur de contrainte de cisaillement développé à McGill, a été conçu et construit pour mesurer les propriétés rhéologiques des polymères fondus. Le débit entier du procédé passe par le rhéomètre, et le temps de réaction est donc plus vite comparé aux rhéometres cours à déviation. La possibilité d'utiliser le rhéomètre en ligne pour l'analyse dynamique mécanique a été étudiée, et des méthodes ont été développées pour obtenir des données de module complexe sur un grand domaine de fréquences par une seule mesure. Des techniques de mesure de viscosité de cisaillement ont été développées ainsi que des algorithmes pour compenser les effets de la pression et de la température du procédé.

Le rhéomètre a été utilisé comme capteur dans une boucle de régulation de la viscosité pour le procédé de viscoréduction de polypropylène. Un modèle de premier ordre avec temps mort a été utilisé pour le modelisation du procédé avec des temps mort de moins de 60 s et une constante de première ordre égale à 15 s. La variation du gain du procédé a été compensée par une variation inverse du gain du contrôlleur pour les types minimisation des variances et proportionel-intégral pour réaliser des temps de stabilisation de 200 s pour des changements de point de consigne de la viscosité et des perturbations du procédé.

#### **Acknowledgements**

I would like to express my deepest appreciation to my supervisors, Professors J.M. Dealy and W.I. Patterson, for their guidance and advice throughout the course of this project. Dr Dealy coordinated the research and provided rheological wisdom, while Dr Patterson supplied direction during the modelling and control stage of the project.

I would like to thank the members of my research group, along with the other students in the polymer engineering group, for stimulating conversation, ideas, and even more advice. In particular, I would like to thank Mark Weber for providing the "Montreal connection" once I left McGill, and Dr Dee Ling for her help in getting this thesis together.

My gratitude also goes out to Dr T.O. Broadhead, who worked on a related project and shared with me the joys of commissioning new equipment. He provided help and advice on both the practical and theoretical aspects of this project. The design of the rheometer was a collaboration between myself and Drs Broadhead, Dealy, Patterson; F.R. Bubic took our ideas and provided the mechanical design and drawings for construction.

Building the rheometer would not have been possible without the considerable efforts of the shop personnel, especially Alain Gagnon, who provided the precision work need to construct the rheometer. Walter Greenland and Charles Dolan also deserve mention for the help they provided every time a crisis arose. Lou Cusmich, our electronics technician, also provided many custom electronic circuits and helped with troubleshooting and general advice throughout the project. Jean Dumont, if he did not already have what was needed, sourced and supplied the many parts required for this project. Andy Krish helped coordinate the building of the extrusion facility and other technical aspects of the project.

Himont Canada, Barber Colman Comapny and Werner and Pfleiderer Corp. supported this work with materials and funding. In particular, I would like to that J. Curry of W&P and Rene Garneau of Himont Canada for their time and technical advice. The Natural Sciences and Engineering Research Council also provided funding for this project.

### Table of Contents

Abstract
Résumé ii
Acknowledgements iii
List of Figures
List of Tables xiii
Nomenclature
1. INTRODUCTION       1         1.1 Process Rheometer Design       2         1.2 Overview of Commercial Process Rheometers       4         1.3 In-line Rheometers       7         1.4 Research Objectives       10
2. THE MCGILL IN-LINE RHEOMETER       12         2.1 Design Principles of the ILR       13         2.2 The Shear Stress Transducer       16         2.2.1 The Disk Spring Design       18         2.2.2 Torsion Beam SST       19         2.4 Rheometer Drive Systems       22         2.4.1 Arbitrary Strain Drive System       22         2.4.2 Steady Shear Drive System       27         2.5 Rheometer Data Acquisition and Control       28         2.6 Rheometer Operating Software       29
3. THE POLYPROPYLENE VISBREAKING PROCESS       31         3.1 Description of Visbreaking Process       32         3.2 Rheological Effects of Visbreaking       36         2.2.1 Determination of MWD from Dynamic Machenical Apply
3.2.1 Determination of NWD from Dynamic Mechanical Analy-         sis       37         3.2.2 Use of the Melt Flow Rate       39         3.3 Process Identification and Control Background       40         3.4 Base Polypropylene Characterization       43         3.5 Peroxide Masterbatch Preparation       45         4 EXPERIMENTAL APPARATUS       48
4. EXPERIMENTAL AFFARATOS

. •

.

	v
4.3 Gravimetric Feeders	52 53
5. DYNAMIC MECHANICAL ANALYSIS USING COMPLEX WAVEFORMS	55
5.1 Introduction	55
5.1.1 Storage and Loss Moduli as Complex Variables	33 57
5.3 Properties of the Discrete Fourier Transform	57 60
5.3.1 Aliasing	63
5.3.2 Time and Frequency Domain Scaling	65
5.3.3 Leakage	65
5.3.4 Alternating versus Simultaneous Data Acquisition	67
5.4 Waveforms of Special Interest	69
5.4.1 PRBS Waveforms	69 70
5.5 A Sample DMA Experiment	12
5.6 1 SST Frequency Response Characteristics	81
5.6.2 Conclusions	84
6. SHEAR VISCOSITY MEASUREMENT TECHNIQUES	85
6.1 Introduction	85
6.2 Pressure Compensation	85 85
6.2.1 Effects of Pressure on the wall stress Calculation	01
tion	92
6 3 Temperature Compensation	97
6.4 Techniques to Improve Sample Renewal	99
6.5 Elements of a Rheometer Measuring Cycle	103
6.6 Rheometer Accuracy and Precision	104
7 DROCESS IDENTIFICATION WITH THE IN-LINE RHEOMETER	107
7.1 Continuous Time Modelling	107
7.1.1 Steady State Control Charts	107
7.1.2 First Order with Dead Time Models	110
7.2 Discrete System Modelling	113
7.2.1 First Order Models with Dead Time	115
7.2.2 Process Noise Model	121
7.3 Rheometer Dynamics	122
7.4 Identification Summary	123
8. PROCESS CONTROL WITH THE IN-LINE RHEOMETER	126
8.1 Proportional-Integral Controller	126

8.1.1 PI Control Simulations	127
8.1.2 Experimental Results: Setpoint Tracking	130
8.2 PI Controller with Gain Scheduling	132
8.2.1 Setpoint Tracking	133
8.2.2 Disturbance Rejection	135
8.3 A Minimum Variance Controller with Gain Scheduling	136
8.3.1 Developing the Minimum Variance Controller	137
8.3.2 Setpoint Tracking	140
8.3.3 Disturbance Rejection	144
8.4 Summary of Control Experiment Results	148
9. CONCLUSIONS AND RECOMMENDATIONS         9.1 Conclusions         9.1.1 The Suitability of the ILR as a Process Rheometer         9.1.2 Control of the Polypropylene Visbreaking Process         9.2 Contributions to Knowledge         9.3 Recommendations and Suggestions for Future Study	150 150 150 151 152 153
REFERENCES	156
Appendix A: Derivation of the MVC Equation, Sample Process Identification Cal tion	cula-
Appendix B: Sample BASIC Programs, SST Calibration Calculations	
Appendix C: Detailed Rheometer Drawings	
Appendix D: Equipment and Peroxide Specifications	

Appendix E: Manuals for BASIC Communications Programs, MACO 8000 Interface (stored on floppy diskette in WP51 format)

:

vi

.

### List of Figures

Figure 1-1 - Cross-section of flow through a tube, with a low viscosity melt flushing out higher viscosity material. The low viscosity material forms a channel down the centre of the tube.	3
Figure 1-2 - Schematic of open capillary process rheometer coupled to a single screw extruder.	5
Figure 1-3 - Schematic of three pump process capillary rheometer. A two pump system is similar, but has no circulation pump.	6
Figure 1-4 - Schematic of Rheometrics On-line Rheometer	8
Figure 1-5 - Schematic of wedge die used by Pabedinskas [11]	9
Figure 2-1 - Schematic of in-line rheometer, where A is the rotating drum, B is the shearing zone and C is the shear stress transducer	12
Figure 2-2 - Rheometer body and removable drive shaft. The shearing drum is mounted on the end of the drive shaft	14
Figure 2-3 - The rotating drum shears the polymer against the face of the SST. The shearing gap is 1 mm in height, 25 mm in width and 51 mm long 1	15
Figure 2-4 - Disk spring shear stress transducer. The disk spring acts as both a pivot for the transducer beam and a seal to prevent polymer from flooding the SST interior.	18
Figure 2-5 - Typical calibration results for disk spring SST. Each weight is repeated four times. The lower range of the transducer is calibrated (weights only to 100 g), since this is where the system operates with PP.	19
Figure 2-6 - Top view of torsion bar transducer, with torsion bars supporting the SST beam in place of the disk spring.	20
Figure 2-7 - Diagram of torsion bar SST, with torsion bars perpendicular to the plane of the drawing. The active face is kept aligned by tightening a set screw when mounting the head J.	20
Figure 2-8 - Calibration data for the torsion bar SST, with and without the shim seal in place.	21

Figure 2-9 - Drive control system for arbitrary strain profile generation.	24
Figure 2-10 - Arbitrary drive system for in-line rheometer. The unit was suspended from the side of the rheometer, supported by the rheometer drive shaft.	25
Figure 2-11 - Sinusoidal strain, 1 Hz, 15% strain amplitude. The strain signal is taken from the position transducer mounted on the end of the drive shaft.	26
Figure 3-1 Schematic of a free radical causing PP chain scission	32
Figure 3-2 Melt Flow Rate vs Initiator Concentration [18]	34
Figure 3-3 MWD of PP at various peroxide concentrations (from Suwanda et al. [19])	35
Figure 3-4 Viscosity curves of polypropylene with various M <sub>w</sub> [18], with viscosity in Pa <sub>5</sub> and shear rate in 1/s	36
Figure 3-5 Effect of MWD on master curves (from Zeichner and Patel [24])	38
Figure 3-6 Correlation of PDI with $M_w/M_n$ (from Zeichner and Patel, [24])	39
Figure 3-7 Storage and loss moduli, complex viscosity and shear viscosity measurements for Profax 6631 polypropylene at 200°C.	43
Figure 4-1: Schematic of the extruder, rheometer and control systems	48
Figure 5-1 - Sinusoidal Strain and Resulting Stress	58
Figure 5-2 - Strain composed of two superposed sine waves and resulting stress response	59
Figure 5-3 - Start-up transients in a dynamic measurement using a multi-sinusoid composite waveform	62
Figure 5-4 - Spurious 5 Hz sine wave from sampling a 100 Hz signal at f <sub>s</sub> =95 Hz	64
Figure 5-5 - The effects of leakage due to assumed periodicity	66
Figure 5-6 - Relative phase shift due to alternating sampling	68

viii

	ix
Figure 5-7 - Sample PRBS waveforms for $n_B = 4,5$	70
Figure 5-8 - DFT of a PRBS, $n_B = 5$ , $\Delta t_B = .5$ s	71
Figure 5-9 - Randomly switched waveform, $p_s = 50\%$ , $N_s = 31$ , $\gamma_s = 15\%$	72
Figure 5-10 - Stress relaxation experiment; silicone putty at 30°C	74
Figure 5-11 - PRBS test: stress and strain results (time domain)	75
Figure 5-12 - Stress and strain: frequency domain results	76
Figure 5-13 - PRBS experiment results compared with single point data from the same sample.	77
Figure 5-14 In-line rheometer PRBS experiment result, Profax 6631, $\Delta t_B = 0.0667 \text{ s}, n_B = 5, f_s = 250 \text{ s}, 517 \text{ data points}. \dots \dots \dots \dots$	78
Figure 5-15 DFT of stress and strain data from Figure 5-14	79
Figure 5-16 G', G" curves calculated from data in Figure 5-14. The points are single point measurements performed on the RDA.	80
Figure 5-17 The magnitude and phase of the G <sup>*</sup> (f) function calculated from the ILR data. Single points are RDA data	81
Figure 5-18 Response of the SST to a step in stress with and without polymer present in the rheometer cavity.	82
Figure 5-19 Frequency analysis of stress step data in Figure 5-18; magnitude of the frequency components.	83
Figure 5-20 Phase difference between ideal step and SST response	83
Figure 6-1 - Regression results: the effect of P and $\Delta P$ on the SST signal. The effect of $\Delta P$ is subtracted from $V_{SST}$ when graphing the P effect in (a), and vice versa when graphing (b).	87
Figure 6-2 Start up transient of SST signal, resin B8 flow stepping from 0 to 6 kg/h, small die on the extruder.	89
Figure 6-3 Sample pressure simulation result modelling the response to a pressure step in the rheometer from 0 to 1.75 MPa	90

Figure	6-4 Sample of the effect of surging on a stress measurement, with $\gamma = 25$ 1/s	91
Figure	6-5 Slit flow, with the pressure flow in the same direction as the drag flow.	92
Figure	6-6 Shear rate profiles of a Newtonian fluid in the gap between two parallel plates, with (solid line) and without (dashed line) a pressure drop. $\gamma \cdot_{drag} = 30$ 1/s, $\Delta P = .62$ MPa	93
Figure	6-7 Shear rate profiles in the rheometer gap	95
Figure	6-8 Finite element simulation of flow through the process rheometer. Drum rotation is clockwise, polymer flow is from left to right. Figure from Broadhead [12].	100
Figure	6-9 Finite element simulation of flow through the process rheometer. Drum rotation is counter-clockwise, polymer flows from left to right. Figure from Broadhead [12]	101
Figure	6-10 Rheometer measuring cycles for identification and control experiments: a) $\Delta t = 15$ s and b) $\Delta t = 25$ s	104
Figure	7-1 - Control graph for visbreaking process, with $\eta$ measured at 3 different shear rates	108
Figure	7-2 - Control graph, viscosity verses peroxide concentration, with single standard deviation error bars	109
Figure	7-3 - Response of the visbreaking process to step changes in the peroxide concentration, $\gamma = 30$ 1/s.	110
Figure	7-4 - A 175 ppm step down in peroxide concentration, with a fitted first order plus dead time model	111
Figure	7-5 - Small change in peroxide concentration, fitted with first order plus dead time model. Noise makes it difficult to determine exactly how much of the response is dead time $(t_d)$ .	1 <b>12</b>
Figure	7-6 - Data from a stochastic identification experiment. The input concentration setpoints are the PRBS waveform in the lower graph, while the upper shows the process response.	116

.

.

х

Figure 7-7 - Process gain $k_p$ as a function of viscosity. Results are compiled from PRBS tests at $\Delta t=13$ , 15 and 25 s	120
Figure 7-8 - Residence time distribution for extruder with and without the rheometer. Data from Chen [48]	123
Figure 8-1 Control diagram of the visbreaking process	127
Figure 8-2 Continuous time process simulation results; the optimal response of the process to a unit step in $\eta_{\text{sept}}$ calculated using the three different error functions and compared with the open loop response	128
Figure 8-3 Process response to viscosity setpoint changes, PI controller with $k_c = .4$ and $\tau_I = 40$ s	131
Figure 8-4 Response of the process to setpoint changes using a PI controller with gain scheduling and flushing effect gain factors, $k_pk_c=.31$ , $\tau_1=40$ s	133
Figure 8-5 Response of process to large and small amplitude setpoint changes, PI controller with gain scheduling and flushing effect gain factors, $k_pk_c=.31$ , $\tau_1=40$ s	134
Figure 8-6 Disturbance rejection of PI controller with gain scheduling, $k_pk_c=.31$ , $\tau_1=40$ s, $\eta_{sept}=800$ Pa s. The actual masterbatch concentration is 1000 ppm.	135
Figure 8-7 Response of the gain scheduled MVC to setpoint changes, $\theta = 0.65$ .	141
Figure 8-8 Response of the gain scheduled MVC to setpoint changes, $\theta = 0.55$ .	142
Figure 8-9 Response of the gain scheduled MVC to setpoint changes, $\theta = 0.75$ .	143
Figure 8-10 Response of the gain scheduled MVC to simulated step disturbances in masterbatch concentration.	145
Figure 8-11 Response of the gain scheduled MVC to changing masterbatch concentrations, from 1000 to 500 ppm and back again. MBCN=1000 ppm, $\theta$ =0.6.	146
Figure 8-12 Response of gain scheduled MVC to changing masterbatch concentration, 500 to 1000 to 500 ppm. MBCN=500 ppm, $\theta$ =0.8	147

xi

Figure A-1 - Process data for a sample analysis, with the peroxide concentration as the manipulated input, and viscosity at 30 1/s as the measured response. Data sampling period $\Delta t = 25s. \dots \dots \dots \dots \dots \dots \dots$	A-7
Figure A-2 - Two graphs generated by the RESID function. The first is the auto- correlation function of the residuals. The second is a cross-correlation between the residuals and the process input.	A-10
Figure A-3 - Auto and cross correlation functions generated by the RESID function for the process and noise model parameters generated by PEM. The dotted lines mark the $3\sigma$ confidence intervals about zero	A-12
Figure B-1 - Geometry of the beam for calibration	B-10

.

xii

.

### List of Tables

Table 3-1 Estimates of $M_w$ and $M_w/M_n$ for Profax 6631 polypropylene before and after extrusion, and at low and high peroxide concentrations. Typical crossover moduli and frequencies are included, in Pa and rad/s respective-	45
ly	45
Table 6-1 Table of y* values calculated for high and low viscosity polypropylene at high and low shear rates and flow rates.	96
Table 6-2 Comparison of ILR response times to step changes in peroxide concentration using forward rotation shearing gap flushing with resptimes for backward/forward technique. (Steps: 100 - 200 ppm and 300 - 400 peroxide.)	onse ppm 102
Table 6-3 - Comparison of viscosity from ILR, SPR and capillary rheometers. The viscosities are listed in Pa's, and are taken at 30 1/s, 209°C. Each result reported for the ILR is an average of 11 measurements, with the standard deviation listed as well.	105
Table 7-1 - Average standard deviations, $k_p$ (from best linear fit) and ratios for data in Figure 7-1	108
Table 7-2 - Model parameters for the first order model (7-1) calculated         for a series of step tests.	113
Table 7-3 - Results from replicate PRBS runs, with $\Delta t = 15$ s, concentration mid- point 125 ppm and a step size of 50 ppm. Parameters are calculated using two full periods of dead time and listed $\pm$ one standard deviation	116
Table 7-4 - Parameters from runs with varying step size, $\Delta t = 15$ s, concentration midpoint 125 ppm. Analyzed using two full periods of dead time, parameters shown with $\pm$ one standard deviation.	117
Table 7-5 Results of experiments conducted with different $\Delta t$ values. <b>f</b> , the number of periods of dead time, is listed with $\Delta t$ .	119
Table 8-1 Continuous time PI controller parameter results from control simula- tions using a first order plus dead time model ( $\tau_p = 16$ s, $k_p = -1$ , $t_d = 56$ s)	129
Table 8-2Values of the gain parameters at various viscosity levels.Thefractions of the reference gains, G, used to determine the linear gainfunction are also displayed.	139

Table 9-1 - Results of fitting process model in equation (A-24) to data in	
Figure A-1 using OE routine	A-9
Table 9-2 - Results of using PEM to fit data to equation (A-27).	A-11

### <u>Nomenclature</u>

a <sub>t</sub> :	White noise signal, zero mean, unit S.D.
A/D:	Analog to Digital
c:	Fractional period of dead time
CRT:	Cathode Ray Tube
DFT:	Discrete Fourier Transform
DMA:	Dynamic Mechanical Analysis
e <sub>t</sub> :	The difference between the process setpoint and the actual value
E <sub>A</sub> :	Activation energy
f:	Number of whole periods of dead time
f <sub>Nyq</sub> :	Nyquist frequency
f <sub>a</sub> :	Alternating sampling frequency
f <sub>s</sub> :	Sampling frequency
Δf:	Frequency step in DFT
F:	Fundamental frequency
FFT:	Fast Fourier Transform
G*:	Complex modulus
G':	Storage modulus
G":	Loss modulus
G <sub>c</sub> :	Cross-over modulus
$\mathbf{G}_{\mathrm{KU}}, \mathbf{G}_{\mathrm{KD}}$ :	Gain factors for the PI controller
h:	Height of shearing gap
I/O:	Input/Output
ILR:	In-line rheometer
ISE:	Integrated square error cost function
IAE:	Integrated absolute error cost function
ITAE: Integ	rated time absolute error cost function
k <sub>c</sub> :	Controller gain
k <sub>p</sub> :	Process gain
L:	Length of shearing gap

.

M <sub>n</sub> :	Number average molecular weight
M <sub>w</sub> :	Weight average molecular weight
$M_w/M_n$ :	Polydispersity
MBCN:	Peroxide concentration in the masterbatch
MFM:	Melt Flow Monitor (Rheometrics)
MI, MFR:	Melt Index, Melt Flow Rate
n <sub>b</sub> :	Degree of PRBS
N:	Number of points or samples in a series
N <sub>b</sub> :	Number of discrete time intervals in a PRBS
P1, P2:	Pressure measurements from ILR, upstream and downstream of the
	measurement zone
P:	Average value of P1, P2
Δ <b>P</b> :	Difference, P1 - P2
PDI:	Polydispersity Index
PI:	Proportional-Integral controller algorithm
ppm:	Parts per million
PRBS:	Pseudo-random binary signal
Q:	Volumetric flow rate
R:	Ideal gas law constant
ROR:	Rheometrics On-line Rheometer
RTD:	Resistance Temperature Device, or Residence Time Distribution
RTR:	Real Time Rheometer (Goettfert)
S.D.:	Standard Deviation
SST:	Shear stress transducer
t:	Time
t <sub>d</sub> :	Dead time
Δt:	Sampling period
Δt <sub>b</sub> :	Minimum discrete time step in a PRBS
Т:	Temperature, or the period of cyclic signal
T <sub>b</sub> :	Period of a PRBS

•

xvi

u:	Peroxide concentration
<b>V</b> :	Volume, or velocity
y*:	Point where Newtonian and power-law shear rate profiles intersect
<b>z</b> -1:	Backwards shift operator
ß:	Compressibility, or power law velocity profile parameter
γ:	Strain
γ₀:	Strain amplitude
γ.	Shear rate
$\dot{\gamma}_{ m app}$ :	Apparent shear rate
δ:	Phase of complex modulus, G <sup>*</sup> ; parameter for discrete model
δ <sub>a</sub> :	Phase shift due to alternating sampling
θ:	Noise parameter in discrete model
η:	Shear viscosity
η*:	Complex viscosity
$\eta_0$ :	Zero shear viscosity
σ:	Shear stress
$\sigma_{ m app}$ :	Apparent shear stress
$\sigma_{w}$ :	Shear stress at the wall
σ <sub>0</sub> :	Shear stress amplitude
$ au_{ m I}$ :	Integral time constant
$ au_{\mathrm{p}}$ :	First order process time constant
ω:	Angular frequency, radians/s
$\omega_1, \omega_2$ :	Gain parameters for discrete model
ω <sub>c</sub> :	Cross-over frequency

xvii

### CHAPTER 1 INTRODUCTION

Recent trends towards improved efficiency and waste reduction in the polymer industry have led to a tightening in the quality control specifications that end-users demand from their suppliers. This has forced polymer producers to search for better ways to control the quality of their products. A major advance has been the incorporation of process rheometers into production lines. This allows the manufacturer to measure the rheological properties of materials while they are being processed, eliminating the time required to send a sample to a laboratory. Typical laboratory measurements take at least thirty minutes; at 20,000 pounds or more per hour, this causes a lot of off-spec polymer to be produced between the time a disturbance enters the system and the time it is detected. Further, any corrective measures taken are based on information that is 30 minutes old.

Process rheometers are currently used mainly for quality control. The response times of these units have only recently been reduced to the point where they can be employed as control sensors. Reactive extrusion processes in particular can benefit from this technology; an extruder will react more quickly than a large reactor, and with a fast process rheometer very good control is possible.

A novel in-line rheometer has been developed at McGill University for use with molten polymers. This rheometer is based on a device called a shear stress transducer (SST) [1,2] that is capable of measuring the local shear stress over a small area of a wall in contact with flowing polymer. This device was first incorporated into a laboratory sliding plate rheometer [3,4] from which came the concepts leading to the development of the in-line unit. The in-line rheometer (ILR) has a fast response to changes in product viscosity, making it an ideal sensor for process control applications.

A polypropylene visbreaking process, in which polypropylene is degraded using an organic peroxide, was chosen to evaluate the capabilities of the ILR as a process control sensor. This reactive extrusion process is relatively simple to control since one variable, the peroxide concentration, overwhelms the effect of other process variables on melt viscosity. The peroxide concentration was manipulated to control the product viscosity, compensating for feedstock fluctuations and process upsets such as changes in peroxide masterbatch concentration.

#### 1.1 Process Rheometer Design Considerations

Most polymer processes depend on indirect or off-line measurements to control the quality of their product. Variables such as temperature or pressure can give immediate knowledge about the state of a process, but provide only indirect information about the characteristics of the polymer itself. Off-line rheological or other property measurements usually require thirty minutes or longer before results are available. An on-line or in-line rheometer is one way to get a fast, direct measurement of product characteristics. Note that "on-line" denotes a rheometer that draws a sample stream from the process, while in an "in-line" rheometer the entire process flow passes through the rheometer. "Off-line" refers to analysis performed in a laboratory.

The challenges in designing a process rheometer that can measure absolute rheological properties are not trivial. The rheometer must be capable of generating a controlled deformation under controlled conditions. A controlled flow is necessary to ensure that true values rather than machine-dependent apparent values of viscosity are obtained, even for highly non-Newtonian melts. The material being tested is highly viscous and often highly elastic, while the process operates at high temperature and pressure. The rheometer must be robust enough to operate without frequent attention in harsh production environments. It should be mechanically simple and easy to disassemble and clean.

Additional problems in rheometer design arise from the nature of the flow of highly viscous materials. Flows of polymer melts are characterized by very low Reynolds numbers and are thus always laminar. The polymer velocity near a wall is very slow relative to velocities near the centre of a channel. Therefore, the centre of a channel will be flushed quickly, while older material will remain near the walls for a long time. This problem becomes even more severe if a low viscosity material is displacing



Figure 1-1 - Cross-section of flow through a tube, with a low viscosity melt flushing out higher viscosity material. The low viscosity material forms a channel down the centre of the tube.

one of a higher viscosity, as shown in Figure 1-1. If the volumetric flow rate is constant, the new, low-viscosity material flowing in the centre of the cavity will exert a lower stress on the old, higher viscosity material near the wall, causing it to flow even more slowly and creating a "channelling" effect. These flow characteristics all act to broaden the residence time distribution of a melt in a rheometer.

The melt flow characteristics affect the rheometer's ability to quickly obtain a representative sample from the process. The length of time required for a rheometer to flush its measurement zone and sample new polymer largely determines its response time to a change in process viscosity. High flow rates are therefore needed to ensure a short response time. This often conflicts with the desire to perform viscosity measurements at low shear rates, where viscosity is more sensitive to the molecular weight distribution. A rheometer must therefore be capable of a range of flow rates to meet both of these requirements. Sampling from the process flow is affected as well; the polymer drawn into the rheometer will tend to be the slower moving material near the wall, while fresher, faster moving material moves down the centre of the process channel. Dead zones in the rheometer where polymer can stagnate and degrade must be avoided. There will be no turbulence to help flush out these zones. Also, if filled materials are to be

tested, all flow channels must be large enough to permit passage of the filler particles without clogging.

Temperature measurement and control of the material itself is another problem. Polymers have a low thermal conductivity and a high viscosity. Due to viscous dissipation, a substantial temperature gradient may exist across the flow. Even measuring the polymer temperature is an uncertain art because of temperature inhomogeneity [5]. Ideally, melt temperature should be known exactly and be uniform throughout a sample for an accurate rheological measurement to be made.

#### 1.2 Overview of Commercial Process Rheometers

A number of commercial process rheometers are currently available, predominately of the on-line configuration. They are used primarily for monitoring polymer quality, although some models have response times fast enough for use as process control sensors. Most models are of the pressure-flow type, although a rotational process rheometer was, at one time, available as well.

The simplest process capillary rheometers are the open system models, which draw a small side stream from the main process flow and use a gear pump to force the melt through a capillary die, as shown in Figure 1-2. The system is open because one end of the capillary is open to the atmosphere, and the polymer leaving the rheometer constitutes a waste stream rather than being returned to the process. The pressure at the inlet of the die is measured, giving the apparent shear stress, while the apparent shear rate is calculated from the volumetric flow rate inferred from the pump speed. Several versions of this type of rheometer can be operated in a constant pressure mode that allows on-line simulation of melt index testing. These rheometers can be made quite small for easy fitting to an existing system and are available with slit dies as well as capillaries. Easy access to the die and pressure transducer allow these systems to be quickly reconfigured to handle a wide range of polymer viscosities. Goettfert [6] and Seiscor [7] both manufacture rheometers of this type.

1110



Figure 1-2 - Schematic of open capillary process rheometer coupled to a single screw extruder.

Although these open system rheometers are simple and robust, they have a number of drawbacks. The first is that the rate of sample renewal in the rheometer is limited by the shear rate of the test being performed. Low shear rate viscosity measurements tend to be more sensitive to the molecular weight distribution than high shear rate viscosities, but involve the lowest flow rates through the capillary. Therefore they also involve the longest transit time to the rheometer through the transfer lines, up to 80 minutes in some cases [8]. This is where most of the response delay comes from for these instruments.

A number of additional problems surface when simulating melt index (MI) measurements. For highly viscous materials, this constant stress test often involves relatively low flow rates through the instrument, leading to slow sample renewal. Also, since the rheometer is running in a constant pressure mode, a change in product melt index results in a change in the speed of the gear pump, which will change the response time of the rheometer (i.e. if the melt index goes from 2 g/10 min to 4 g/10 min, the flow rate through the rheometer is doubled). This introduces a nonlinearity into the rheometer response with which process controllers have difficulty dealing: a variable process time constant.

.

Another disadvantage of the open system is the waste stream generated by the unit. Though usually quite small compared to the amount of polymer flowing through the process, it does require occasional disposal by an operator and can lead to housekeeping problems in the production area. A third drawback may exist for polymer systems that contain volatile solvents or residual monomer. These components can leave the melt phase and form bubbles in the material as the pressure in the capillary decreases towards atmospheric, disturbing the viscosity measurement.

A "closed" system results when a second gear pump is added to the open system to return the tested melt back to the system. The second gear pump is controlled in one of two ways; either it rotates at a fixed speed relative to first gear pump, or it is controlled by a pressure transducer to maintain a fixed pressure at the exit of the die. While this arrangement eliminates the waste stream from the process, sample renewal in the transfer lines and the rheometer is still limited by the test shear rate selected for the capillary.



P: Pressure

T: Melt Temperature

G1: Measuring Pump

- G2: Return Pump
- G3: Circulation Pump
- $\Leftrightarrow$ : Polymer Flow



Two approaches have been taken to improving the response times of closed systems. The first is embodied in a slit die unit manufactured by Rheometrics [9], called

the Melt Flow Monitor (MFM). This unit is mounted very close to the process stream, so that the transfer lines to the measurement zone are kept as short as possible. While this improves the response, it is still dependent on the flow rate through the test zone (i.e. the test shear rate). Thus, the response to constant pressure measurements will be a function of material properties. The second approach is to incorporate a recirculation loop with a third gear pump to increase the polymer flow rate through the transfer lines as shown in Figure 1-3. Goettfert [8] has implemented this approach in their Real Time Rheometer (RTR), which is available with slit or capillary die geometries. This method allows independent control of the polymer flow through the transfer lines. Only the relatively small volume in the test section itself is flushed at the test flow rate, while the recirculation loop maintains a much larger flow rate in the transfer lines (from 10 to 100 times faster). When running in MI mode (constant pressure), the response of the RTR can be made practically independent of the flow properties of the material being measured. The length of the transfer lines also becomes a less critical issue; this is important when the unit is installed on an existing system and cannot be mounted close to the process stream.

Another commercial process rheometer, the Rheometrics On-line Rheometer (ROR) uses a Couette concentric cylinder geometry to perform dynamic mechanical analysis (DMA). A gear pump draws a small side stream from the process and feeds it into the rheometer (see Figure 1-4), where it flushes out the old sample. The outer cylinder oscillates, and the torque generated on the inner cylinder is measured. Sampling from the process must be halted during the measurement so that the through-flow will not interfere with the measurement [10]. This instrument is complex and difficult to disassemble and clean. It also suffers from a slow response to process fluctuations due to the long time necessary to flush out the concentric cylinder test section.

#### 1.3 In-line Rheometers

An in-line rheometer is placed directly in the main process flow. The entire process stream flows through the instrument rather than only a small sample stream,



Figure 1-4 - Schematic of Rheometrics On-line Rheometer

presenting a number of advantages. Firstly, the entire process flow is used to flush out the rheometer, greatly reducing the amount of time necessary to renew polymer in the measurement zone and increasing the speed of the rheometer response to viscosity fluctuations. Also, no high shear gear pump is necessary to draw off a sample, reducing shear history affects for shear-sensitive or fibre-filled materials. A third advantage is that in-line rheometers operate at the ambient process pressure. Many polymers contain volatile solvents and monomers that will come out of solution and create bubbles in the material when the pressure drops below a certain value. While this can happen in capillary measurements exhausting to the atmosphere, the measurement zone of the ILR is completely enclosed and pressurized.

In-line rheometers also have some inherent disadvantages. Since they are not isolated from the process, they are exposed to the fluctuations in pressure, temperature and flow rate that inevitably occur. The same process flow that provides sample renewal must not interfere with the viscosity measurement itself. Also, it is not practical to perform any temperature conditioning of the melt before testing; tests must be performed at whatever temperature the process imposes.

Attempts have been made to measure rheological properties in-line by monitoring the pressure drop as the melt flows through a given section of the process. While the pressure drop depends strongly on the rheological properties of the polymer, it also depends on the process flow rate, which is usually not precisely known. Also, many disturbances both upstream and downstream of the pressure measurement points will affect the reading; a shift in the pressure could be due to changes in the product, the flow rate, or possibly some downstream equipment that affects the process pressure distribution. Pressure readings also contain a high frequency noise component, due to high



Figure 1-5 - Schematic of wedge die used by Pabedinskas [11].

frequency pressure fluctuations (such as those caused by the turning of an extruder screw), machine vibrations, and electronic noise (due to the millivolt signal levels of strain gauge pressure transducers).

Pabedinskas et al. [11] used an extruder to feed a wedge-shaped slit die with three pressure transducers, as shown in Figure 1-5. The polymer experiences an increasing shear rate as it moves down the die. Pressure transducers were positioned so that the pressure drops  $\Delta P_{1.2}$  and  $\Delta P_{2.3}$  were approximately equal for the polypropylene that they were using. The data from the pressure transducers were then used to calculate powerlaw viscosity coefficients. An off-line measurement of the flow rate through the extruder was necessary to calculate the shear rate. Since the pressure transducers are incorporated in the die wall, a Bagley type entrance correction is not necessary. However, the polymer never reaches a steady-state flow, since the shear rate is increasing constantly as the polymer moves down the die. The effect of the non-steady-state shear would have to be determined for a specific polymer before this method could be used for true viscosity measurements.

#### 1.4 Research\_Objectives

The objectives of this research project were as follows:

- 1. To design, build and evaluate an in-line process rheometer (ILR) capable of absolute rheological measurements over a range of shear rates.
- 2. To characterize the dynamic behaviour of the ILR to changes in the rheology of the process stream.
- 3. To employ the ILR as a rheological sensor to control a reactive extrusion process.
- 4. To investigate several control algorithms for the control of product viscosity.

The major thrust of this project was to investigate the feasibility of using a process rheometer incorporating a shear stress transducer to make absolute (as opposed to apparent) rheological measurements. Such a rheometer was designed, built, and evaluated as a sensor to provide closed loop control for a reactive extrusion operation. The rheometer was of the in-line type, to realize the short response time inherent in this type of design, and was able to perform oscillatory as well as steady shear measurements. To this end, a motion control system capable of generating the arbitrary strains necessary for DMA measurements was also designed and assembled.

Polypropylene visbreaking was the reactive extrusion process selected to evaluate the rheometer as a control sensor. It was deemed desirable for the rheometer to detect changes in the molecular weight distribution by means of DMA measurements, and then to use this information to control the process. An alternative was to use viscosity setpoint control. To implement the process, a 30 mm twin-screw extruder was purchased and installed along with two gravimetric feeders to control the feed streams to the process. Several control algorithms were investigated: a PI controller, for comparison with previous work by other groups; and a minimum variance controller, to see if model-based dead time compensation significantly improved the controller performance.

The first chapters of this thesis introduce the thesis project, and describe the inline rheometer, experimental setup and polypropylene visbreaking process. The methodology to perform DMA and shear viscosity measurements is developed in chapters Five and Six. Chapter Seven presents the results of process identification and rheometer characterization experiments. Chapter Eight discusses the implementation of the process controllers employed to regulate product viscosity, and the experimental results obtained when testing the effectiveness of these controllers. Finally, chapter Nine contains the conclusions and recommendations for future work.

### CHAPTER 2 THE MCGILL IN-LINE RHEOMETER

The in-line rheometer developed for this project uses a shear stress transducer (SST) to measure the wall shear stress generated by a melt which is sheared in a concentric cylinder geometry. As shown in Figure 2-1, a rotating drum provides the shearing action, but the radius of curvature is great enough that parallel plate geometry may be assumed for modelling purposes. The shearing drum can be rotated at constant



Figure 2-1 - Schematic of in-line rheometer, where A is the rotating drum, B is the shearing zone and C is the shear stress transducer.

speed for steady shear viscosity measurements, or it can be oscillated for dynamic mechanical tests. The wall shear stress at the midpoint of the measurement zone is measured by the SST; since it is a measurement of the local stress, no end or edge effects are involved. Melt thermocouples are used to record polymer temperatures so that a temperature compensation algorithm can correct viscosity data to a reference temperature if desired.

The measurement zone is formed between the top wall of the rheometer cavity and the drive shaft of the motion control system. The shaft, the end of which forms the shearing drum A in Figure 2-1, is a separate assembly from the main body; it can be removed to gain easy access to the interior of the rheometer (see Figure 2-2). The shearing gap has a very small flow cross-section relative to that of the main cavity of the rheometer, only about 3% of the total area; there is thus only a very small amount of pressure-driven flow through the gap. Two pressure transducers are positioned to monitor the pressure drop across the measurement zone (P1 and P2 in Figure 2-1) so that this pressure flow can be taken into account in viscosity calculations.

The rheometer employs the drag flow generated by the rotating drum to replace the polymer in the shearing gap with melt from the main flow. Shear rates from 3 to 30 1/s can be produced using the steady shear drive system. A drive system capable of providing arbitrary strain waveforms at low amplitudes (less than .1 strain units) and high frequency (over 100 rad/s) is employed for dynamic mechanical experiments.

This chapter deals with the mechanical design of the in-line rheometer and its major components.

#### 2.1 Design Principles of the ILR

The design of the rheometer incorporated many new ideas and required the resolution of a number of conflicting design objectives. The most important objectives are discussed below, along with the resolutions reached. The design team consisted of J.M Dealy, F.R. Bubic, T.O. Broadhead and the author.

The main cavity of the rheometer body should be as small as possible in order to minimize the residence time of the polymer in the instrument. However, a high pressure gradient and flow rate across the measurement zone could interfere with the process measurement; for this reason, a large cross-section is desirable where the measurement is being performed. Other general criteria are that there be no dead zones or places where one might expect recirculation, and that all corners be kept as smooth as possible to facilitate polymer flow.

The body was designed with a cylindrical conduit to bring the polymer into the measurement zone (the region between P1 and P2 in Figure 2-1, or between the pressure



Figure 2-2 - Rheometer body and removable drive shaft. The shearing drum is mounted on the end of the drive shaft.

ports shown in Figure 2-2). The cross-section then expands to accommodate the rotating drum and to allow room for the polymer to flow around the drum with minimal pressure drop. The cross-section then contracts back to a circular conduit as the polymer leaves the rheometer. The length of the entrance conduit was kept as short as possible, leaving just enough space for the bolts that attach the rheometer flange to the extruder face. Interior edges are as smooth as possible to reduce abrupt changes in flow direction. The volume of the entrance conduit is  $60 \text{ cm}^3$ , while that of the main cavity is approximately  $50 \text{ cm}^3$ . A polymer flow rate of 12 kg/h corresponds to a volumetric flow rate of  $4.5 \text{ cm}^3$ /s. At this rate, and assuming plug flow as a first approximation, it takes roughly 13 seconds for polymer leaving the extruder to reach the measurement zone.

The selection of the size of the shearing gap was another compromise. A large gap gives good motion control (due to larger motions) at lower shear rates, and better melt sampling due to higher drag flow rates. A smaller gap gives better temperature uniformity in the sample and less flow due to the pressure drop along the gap to interfere with the measurement. The gap is also wide compared with the height to reduce edge effects and produce more uniform shearing across the sample. A gap height of 1 mm was chosen; this is only 4% of the 25 mm radius of the shearing drum, making valid the



Figure 2-3 - The rotating drum shears the polymer against the face of the SST. The shearing gap is 1 mm in height, 25 mm in width and 51 mm long.

assumption of parallel plate geometry in the measuring zone. The width of the measuring slit is 25 mm, giving a width to height ratio of 25. The length of the shearing zone divided by the gap height is 51 and, as shown in Figure 2-3, the SST is mounted in the centre of this zone. The polymer must thus undergo approximately 25 strain units of shear before measurement, ample for the melt to achieve fully developed flow.

A number of designs were considered for the rotating drum. It could have a constant diameter or dual diameters to give two different gaps. A screw flight could be added to one side of the drum to help flush new polymer into the gap. It was decided to use a single diameter drum, with design modifications to be made later if desired. The drum was machined as an annulus which slid onto a keyway on the end of the drive shaft. In this way, the drum could be easily modified, or a new drum mounted with a minimum of effort.
Temperature control of the rheometer was another problem. To maintain the most even temperature throughout the rheometer, temperature gradients had to be minimized. The rheometer was carefully insulated, and strip heaters mounted on the exterior of the rheometer (rather than cartridge heaters inserted in the metal) were used to effect temperature control. The control thermocouple was mounted in the metal next to the SST, about 5 mm from the measurement zone. The SST itself was treated as a separate heat zone; the baseline signal from the capacitance probe was very sensitive to temperature fluctuations, so good control was mandatory.

The rotating drum presented another problem. It was inserted into the polymer stream and its temperature could not be directly controlled. Since the drum is mounted on the end of a steel shaft that extends outside of the rheometer to the motion control system, it was known that a large temperature gradient would exist along the length of the shaft. The drum would thus draw heat directly from the measuring zone, where temperature control was most important. A separate heater was therefore installed in the shaft housing, with brass bushings transferring the heat to the rotating shaft. In this way the portion of the shaft within the rheometer was kept at the same temperature as the rheometer body. In addition, a hole was bored down the length of the shaft so that a resistance temperature device (RTD) probe could be inserted. The temperature of the shearing drum could then be monitored, if not directly controlled, while stationary.

### 2.2 The Shear Stress Transducer

The basic measuring principle of the SST is to convert a shear force into a small deflection, which is then measured by means of a capacitance probe. The active face of the transducer is formed by the end of a beam that is supported by a spring near its midpoint. The spring acts as a pivot, so that when the polymer exerts a shear force on the active face, the beam undergoes an angular deflection about the pivot point. This deflection is measured at the top of the beam by a sensitive capacitance probe, which converts the distance from the probe tip to the target on the beam to a voltage that can be read by a data acquisition board. The deflections in the transducer are very small; the

full scale range of the capacitance probe is 10 V for 1 mil (.001 inches, or  $2.54 \times 10^{-5}$  m), and the actual beam displacements are only a fraction of this. Weights were suspended from the beam through ports for calibration, simulating shearing forces; this allows determination of the spring constant. In practice, rather than calculating an actual spring constant, the SST output signal for a known shear force (as simulated by a suspended weight) is determined directly in the calibration (see Appendix B). This ensures that the capacitance probe electronics are included in the SST calibration; the probe calibration does not have to be checked separately so long as it remains linear.

The temperature of the SST is controlled using a heater band around the housing, with the temperature sensed using a washer thermocouple mounted at the top of the housing. The entire SST is then enclosed in insulation. The baseline signal from the SST is very dependent on the housing temperature. Small changes in this temperature can cause minute changes in the distance between the tip of the capacitance probe and the beam target due to thermal expansion in the housing and the probe, causing the baseline to wander. Very short heater cycles (2 seconds) were used to avoid surges of heat from the temperature controller, which would cause cyclical baseline variations of up to 500 mV<sub>PP</sub> when left set to 20 s, the value used for the extruder barrel zones.

One disadvantage of this design is that there is a small gap around the active face to allow deflection. The lack of a seal at this point means that polymer can leak into the interior of the SST. A seal is made at the pivot point, but the lower cavity of the transducer fills with polymer and must be periodically flushed to prevent problems due to polymer degradation. A channel is thus provided from the rheometer cavity to the exterior of the rheometer body. This drain allows flow through the bottom section, and has a manual throttle to control the flow rate at varying system pressures and polymer viscosities. However, the drain was found to interfere with the SST performance. The flow through the gap around the active face disturbed the shear flow across the face, causing offsets and incorrect readings. It was found that, for the polymers employed for this project, a single flush per day was sufficient to keep degraded material from accumulating. The polymer in the transducer cavity was not exposed to oxygen and thus degraded very slowly.

### 2.2.1 The Disk Spring Design

The disk spring SST uses a beam supported midway down the shaft by a disk spring, as shown in Figure 2-4. The stiffness of the spring, and hence the sensitivity of the transducer, are controlled by the thickness and the inner and outer diameters of the spring membrane. The disk spring also functions as a seal; the bottom of the SST fills with polymer until it reaches the spring.



Figure 2-4 - Disk spring shear stress transducer. The disk spring acts as both a pivot for the transducer beam and a seal to prevent polymer from flooding the SST interior.

This transducer design has been successfully used in the ILR by Broadhead [12], but has a number of drawbacks. First, the beam is not constrained to pivot only in the direction of the flow. The disk spring allows full motion in the plane parallel to the shearing face, in both the direction of the polymer flow and perpendicular to this direction. Secondly, and more importantly, this SST design is sensitive to the absolute pressure in the rheometer. The polymer exerts a normal force on the face of the transducer beam and on the disk spring, causing the beam to deflect axially. The tip of the capacitance probe is not precisely perpendicular with the target on the beam stem, causing a change in the baseline of the SST signal when the beam is deflected along its axis. Pressure fluctuations therefore cause fluctuations in the transducer signal (see section 6.2.1 for more details).

A third problem is the sensitivity of the disk spring SST. The calibration value (see Figure 2-5) was found to be 16.5 kPa/V, giving a full scale range of 165 kPa (or  $\pm 83$  kPa for oscillating stresses). This is much stiffer than is required for the



Figure 2-5 - Typical calibration results for disk spring SST. Each weight is repeated four times. The lower range of the transducer is calibrated (weights only to 100 g), since this is where the system operates with PP.

polypropylene used in this study. Increasing the SST sensitivity means weakening the disk spring to allow it to respond to smaller forces. Unfortunately, this will also increase the amount of vertical beam deflection due to the pressure in the rheometer, limiting the range of operation of the transducer.

## 2.2.2 Torsion Beam SST

In order to restrict the motion of the beam to the direction of the polymer flow, torsion bars were used rather than a disk spring to provide the pivoting action (see Figure 2-6). The beam is now compliant in response to stress perpendicular to the torsion arms (in the shearing direction) but very stiff in the direction parallel to the arms (perpendicular to shearing, to the left or right in Figure 2-6). The arms were made very



Figure 2-6 - Top view of torsion bar transducer, with torsion bars supporting the SST beam in place of the disk spring.

narrow in the direction of melt flow and very thick axially. This was to reduce the vertical motion of the beam due to normal pressure without reducing the sensitivity of the SST to shear stress. Figure 2-7 shows an exploded view of the transducer beam, illustrating how it is assembled. The beam itself is mounted in the transducer housing in the same manner as the disk spring transducer (Figure 2-4), with the outer ring **D** clamped between the housing and the rheometer body.



Figure 2-7 - Diagram of torsion bar SST, with torsion bars perpendicular to the plane of the drawing. The active face is kept aligned by tightening a set screw when mounting the head J.

The removal of the disk spring meant another method had to be used to seal the interior of the transducer against the polymer inflow. A membrane made of brass shim stock (Figure 2-7 F) was mounted below the torsion arms, sealed with a washer and nut (Figure 2-7, G, H and I) to the beam in the centre, and clamped in the housing around the outside. It was assumed that the shim stock would make a negligible contribution to the spring constant while preventing the polymer from entering the SST. A free floating support washer (Figure 2-7 E) was placed behind the shim seal to provide mechanical strength so that the seal could withstand process pressures.

The torsion bar SST was designed to have a 75 kPa full range, twice as sensitive as the disk spring. At the same time, the torsion bar design increased the axial stiffness of the SST by a factor of ten. Initial experiments with the new SST, without the shim seal in place or any polymer present, showed an average calibration of 7.9 kPa/V, very close to the design value. Unfortunately, as seen in Figure 2-8, the addition of the shim



Figure 2-8 - Calibration data for the torsion bar SST, with and without the shim seal in place.

seal considerably decreased the SST sensitivity. Inserting the support ring behind the seal caused a further, drastic change in the calibration constant, to almost triple the design value. In further tests, the calibration of the fully assembled transducer fluctuated

between 15 and 22 kPa/V, changing randomly every time it was reassembled. Once assembled and mounted, however, the calibration remained constant for the duration of any experiments performed.

The SST performed well during viscosity tests with polymer stationary in the rheometer. However, once flow began and the pressure in the rheometer rose, the SST baseline signal moved off-scale. While the design of the torsion bars prevented appreciable vertical motion of the beam, the action of the pressure on the shim seal caused an unbalanced force that forced the beam off centre, in most cases beyond the range of the capacitance probe.

In conclusion, the torsion bar SST was very sensitive to both the absolute melt pressure in the rheometer and the assembly of the SST. No reliable method of assembling the SST was found so that the baseline signal would stay within range once pressure built up in the rheometer. This made the SST unsuitable for use during processing; it was decided to use the disk spring design transducer instead for the process experiments. While less sensitive than desired, the resolution of the system was sufficient for the viscosity ranges encountered in this project.

# 2.4 Rheometer Drive Systems

Two drive systems were available for the rheometer, and are discussed in detail in the following sections. The first was capable of generating arbitrary strain waveforms suitable for dynamic mechanical analysis (DMA) experiments. The second was designed by Broadhead [12] for uni-directional steady shear experiments. It was modified to produce bi-directional motion and used for steady shear viscosity measurements.

## 2.4.1 Arbitrary Strain Drive System for DMA Experiments

A number of design criteria were set for the DMA strain drive system. It had to be bi-directional and capable of generating strains useful for DMA experiments at high frequencies (up to 20 Hz); sine, sum of sines and PRBS (pseudo-random binary signal) waveforms are typical examples. The strain motions also had to have small amplitudes, on the order of .1 to .2 strain units, to remain within the linear viscoelastic limits of the material being tested. Finally, the system had to be capable of continuous rotation (steady shear) in order to flush material from the shearing gap and draw new polymer in to be tested. All of these motions were to be fully controllable from the rheometer PC, and an accurate strain signal was to be available to the computer; any distortion of the actual strain profile from the ideal waveform had to be measured so that it could be accounted for in data analysis.

High frequency motions require high acceleration rates and demand high torques from the drive motor. An AC synchronous torque motor, model 2106-B, from Industrial Drives [13] was used to generate the strain profiles. It was rated to continuously provide 8.1 Nm at 5250 RPM, with peak torques of up to 40 Nm., and was capable of delivering high acceleration rates with a smooth torque output even at low speeds. An analog velocity signal, -10 to 10 volts corresponding to -5250 to 5250 rpm, was used to control the speed, so that strain profiles had to be differentiated before being sent to the drive system. A 12 bit digital position signal was generated by a brushless resolver mounted in the motor. Unfortunately, the 12-bit resolution of the signal was not fine enough to record the strain, giving only 26 quanta (or codes) per strain unit in the rheometer measurement zone (with most strain waveforms to be on the order of .1 to .2 strain units in amplitude).

In order to measure the strain, an angular position transducer (Appendix D) was employed. It was mounted on the end of the drive shaft and directly measured the strain over a 20° arc of rotation, which translated to 8.73 strain units in the rheometer. The midpoint of the 20° arc occurred when the transducer was emitting a 4.572 V signal; the shaft position was centred at this position before measurements were performed. The factory calibrated sensitivity was 306.3 mV/degree. This corresponds to a 0.7 V/strain unit output, or 288 quanta/strain unit when the signal is read by the 12-bit A/D data acquisition board. Distortions of the strain due to transducer frequency response and phase lag were negligible below 20 Hz, and the linearity of the reading was  $\pm 0.5\%$  of full scale.

· · .

The desired strain profile was differentiated in the PC to obtain the shear rate profile and fed point by point to a Wavetek Model 75-ARB Arbitrary Waveform Generator (Appendix D) through a serial communications link. Point by point programming of the Wavetek, which was capable of 12 bit vertical resolution for up to 8192 horizontal points, allowed the use of PRBS and other non-standard strain profiles for DMA measurements (see section 5.4).

Figure 2-9 is a schematic of the drive control system. The PC would calculate a digital strain rate profile from the strain profile and load it into the Wavetek through a serial connection. On command from the PC, the Wavetek would send the analog



Figure 2-9 - Drive control system for arbitrary strain profile generation.

velocity signal to the motor controller, which would cause the drive system to perform the desired strain motion. A voltage divider was used to reduce the analog signal by five times, giving the Wavetek better resolution at low signal levels; the minimum waveform amplitude from the Wavetek was 5 mV. The position sensor monitored the displacement and fed this analog signal back to the computer through its data acquisition board for analysis.

It was decided not to use a gearbox to link the drive motor with the shaft from the rheometer shearing drum to avoid play and backlash in the system during bidirectional





motion. Velocity control of the torque motor was fine enough that direct connection was possible, but finally a chain drive system was selected. This allowed the motor to be mounted underneath the rheometer, as shown in Figure 2-10. This reduced the torsional load of the rheometer on the extruder mounting flange and was less prone to problems with vibrations compared with the direct connect option. A three-to-one gear ratio was employed to improve the accuracy of the displacement control; any ratio higher than this would have resulted in extremely large drive gears. With the chain under a constant tension, there is no slack or play in the links. In the theoretical design study [14], the total displacement error due to elastic deformation of the chain and play in the rollers was calculated to be 0.25% of a 1° oscillation at 20 Hz. Also, the estimated maximum torque required for this oscillation (due to polymer shear, seals and system inertia) was 5.1 N·m, well within the capabilities of the drive motor.

The position sensor for strain feedback was mounted on the end of the rheometer shaft. One problem the design study pointed out was that the shaft would twist elastically during oscillation, since the rotating force was applied at one end while most of the

25

resistance occurred at the other. It was estimated that a  $.02^{\circ}$  to  $.03^{\circ}$  twist would occur which would not affect the amplitude of the waveform but would introduce a phase lag into the strain measurement. The amplitude of the twist would be largely independent of the frequency of the oscillation and the material being tested, since over 60% of the motor torque is required to overcome the friction of the shaft seals, which was constant. A correction algorithm could have been developed to correct for this phase error except that it was found to be negligible compared to other problems with the DMA measurement (see section 5.6).



Figure 2-11 - Sinusoidal strain, 1 Hz, 15% strain amplitude. The strain signal is taken from the position transducer mounted on the end of the drive shaft.

Overall, the drive system worked well. A typical oscillation sampled at 500 Hz is displayed in Figure 2-11, showing little distortion and a very clean signal. A pair of matched, linear-phase anti-aliasing filters (with a cut-off frequency of 40 Hz) were used on the analog stress and strain signals to remove high frequency noise before data acquisition. This prevented harmonics at frequencies above the Nyquist frequency ( $f_{Nyq}=250$  Hz in this case) from being incorrectly added to harmonics in the range of interest during FFT analysis (see section 5.3.1). The amplitude of the generated strain is small enough to be within the LVE limits of the polypropylene being tested, and the

system resolution at this strain level is quite good. A sample PRBS strain profile, shown in Figure 5-14, is displayed and analyzed in section 5.6.

The drive system was also capable of continuous motion for steady shear measurements; it simply had to send a constant voltage signal to the motor controller. Continuous rotation to pull fresh polymer into the shearing gap was easily accomplished. Using this drive system to perform a steady shear viscosity measurement was not, however, feasible. A good velocity feedback signal was not available from the controller. For the shear rate ranges desired in this project, the feedback velocity signal was on the same order of magnitude as the system noise. An accurate shear viscosity measurement was not possible without precise knowledge of the motor speed.

#### 2.4.2 Steady Shear Drive System

Steady shear measurements were performed using a drive system initially developed by Broadhead [12], modified to perform bi-directional shearing. The 3/4 hp (560 W) motor is slung beneath the rheometer in the same manner as with the oscillatory unit, and drives the shaft through a belt driven gear box. It offers over a decade of shear rate range, from 3 to 35 1/s, controlled by a 0-10 V signal from a D/A converter in the rheometer PC. Motor speed control is accurate to  $\pm 0.5\%$  of full scale. A tachometer provides a velocity feedback signal, again in the form of a 0-10 V signal monitored by the A/D board in the PC. Both the setpoint and tachometer signals were calibrated on a daily basis to ensure accurate results.

In order to perform bi-directional shear, the drive system was modified so that the motor direction could be reversed. An electro-mechanical control relay was used to reverse the polarity of the field current in the drive motor. This relay could be switched from the rheometer PC, allowing software control of the direction of the motor. This feature was added to enable the backwards flushing routine discussed in section 6.4.

### 2.5 Rheometer Data Acquisition and Control

The rheometer PC was equipped with a Data Translation DT2801-A multi-function I/O board (Appendix D). This board has 16 single-ended (signals with a common ground), 12-bit analog to digital channels, which can also be configured as 8 differential channels (where the input is the difference between two single-ended channels). The latter configuration was chosen for this project, since it is more resistant to interference by noise. It has software selectable gains and is capable of sampling at speeds up to 27.5 kHz. The board also has two 12-bit digital to analog output channels and two 8-bit digital I/O ports.

The DT-2801-A was initially driven by a software package from Data Translation called PC-LAB, which provided functions and subroutines to control the board functions (i.e. setting sampling rates, specifying channels to sample, etc.). This software was not fully compatible with the QuickBASIC version 4.5 used for software development in this project. A set of subroutines were written using QuickBASIC that directly addressed the board. These routines were called upon to perform the actual data acquisition, as well as control the analog outputs and digital I/O ports. A manual has been written "DTDRV Version 2.2 DT-2801-A Data Acquisition Routines" (see Appendix E), which lists the routines and explains all of their functions.

With the exception of temperature, all functions of the rheometer were controlled by the PC through the DT2801-A board. Four analog to digital channels were used to monitor the SST output, the rheometer strain or strain rate (depending on the drive system used) and two pressure signals, P1 and P2, which allowed calculation of the pressure drop across the measurement zone. During baseline and shearing measurements, the analog signals were sampled at the speed of the internal PC clock, about 18.2 Hz. The DT2801-A board samples its analog input ports in a serial fashion, one after the other, rather than capturing all ports simultaneously (see Appendix E, DTDRV Manual). The sampling frequency of the board was therefore set high enough (25 kHz) that the four analog signals were sampled essentially simultaneously (within 0.16 milliseconds). Along with the data acquisition, a 0-10 V digital to analog output channel was used to control the speed of the constant shear drive motor, while a single bit from a digital output port controlled the direction of the drive motor for reverse shearing experiments.

Temperature monitoring and control for the rheometer were provided by the MACO 8000 control system used to operate the extruder. The pressure transducers P1 and P2 were connected to the MACO system as well as read by the PC, so that the MACO 8000 could perform over and under pressure alarming. Further details on the MACO 8000 can be found in sections 4.2 and 4.4.

## 2.6 Rheometer Operating Software

A large number of programs were written to control the rheometer and the extruder. Typical examples would be a program to measure the viscosity while moderating the feeders to inject a PRBS disturbance into the system, or implementing a minimum variance controller that would adjust the feeder rates to keep the measured viscosity close to a viscosity setpoint. While each type of experiment required a different program, they all had a similar structure and were built around a core of subroutines.

Each program started with a list of constants, including calibration constants and experimental parameters. This made it simple to modify parameters to run variations on experiments. This was followed by initialization routines for the data acquisition board, MACO 8000 system (see section 4.4) and data archive files. The main program was divided into two parts. The first would control the rheometer, making viscosity measurements (see section 6.5) and recording the results to file and to the PC screen. The second part would control the process. This involved modifying the feed peroxide concentration by adjusting the feeder setpoints, either in response to changes requested by a controller or to inject a disturbance into the system. The PC system clock was used to control the timing of viscosity measurements and control actions (control actions were not necessarily performed every time a measurement was taken).

Aside from the experiment programs, a large number of smaller utility programs were also written. These performed tasks such as SST calibration and programming

waveforms into the Wavetek waveform generator. Sample listings of programs can be found in Appendix B.

Ц.

2

# CHAPTER 3 THE POLYPROPYLENE VISBREAKING PROCESS

Polypropylene, with a density of around 900 kg/m<sup>3</sup>, is the lightest of the commercially available thermoplastics. This low density, giving the most parts per unit weight, along with other advantages, such as good high temperature resistance (can be used continuously at temperatures over 100°C), high chemical resistance, good dimensional stability and mechanical properties, and the best contact and see-through clarity of the polyolefins, has contributed to polypropylene's continuously growing market in recent years. Polypropylene can be blended with other polymers and/or fillers to give final products having a wide range of properties, allowing optimization for specific applications. The packaging and textile industries are currently the largest polypropylene consumers, but large inroads into the extrusion and blow and injection moulding markets have recently been made, especially with the introduction of "controlled rheology" resins.

Commercial polypropylene resins made using heterogeneous Ziegler-Natta catalyst systems [15] have weight average molecular weights ( $M_w$ ) in the range of 3 to 7 × 10<sup>5</sup> and broad molecular weight distributions (polydispersity ratios  $M_w/M_n$  between 5 and 20) with a high molecular weight tail [16]. The broad MWD contributes to a high degree of molecular orientation during processing. This can lead to problems, especially for injection moulding, where shrinkage and warping can occur as a moulded part is cooled. It has been found, however, that controlled degradation of the polypropylene before processing reduces the breadth of the MWD and lowers the viscosity without markedly impairing the resin's mechanical properties [17]. The flexural modulus of polypropylene is only slightly reduced after degradation, with over 90% retention when the melt flow rate (MFR) is reduced from 3 to 126 g/10 min [18]. The most negatively influenced property is toughness, making the polymer prone to fracture at notches; this difficulty can be minimized by proper part design. The reduced viscous and elastic properties give the resin better flow properties and decrease the shear stress during processing. This, along with a narrower MWD, reduces molecular orientation, shrinking and warpage.

The plastics industry requires a wide range of polypropylene grades, from MFR  $\approx 1.5$  g/10 min for extrusion blow moulding, to MFR  $\approx 30$  g/10 min for high speed injection, to MFR  $\approx 40$  g/10 min or considerably higher for films and fibre production. The visbreaking process offers a flexible alternative to polypropylene producers. Rather than producing small batches of specific grades, a large quantity of a standard bulk polypropylene with a high molecular weight can be polymerized. This polymer can then be tailored to particular specifications using the visbreaking process. Good control of the process would ensure product uniformity within a batch, and grade changeovers would be simple and fast with minimal waste material.

### 3.1 Description of Visbreaking Process

There are two frequently used methods of degrading polypropylene in an extruder, thermo-mechanical and chemical. Two identical polypropylene samples degraded from one MFR to another, one thermo-mechanically and the other chemically, will have virtually identical rheology [10]. This indicates that both processes operate on the polymer in much the same fashion, even if they use different methods to break the polypropylene molecule. Thermal degradation is negligible below 270°C, and mechanical degradation is extremely energy intensive; for these reasons free radical chemical degradation is the process favoured by industry.

Figure 3-1 Schematic of a free radical causing PP chain scission

Visbreaking is a reactive extrusion process that involves mixing and reacting polypropylene with a source of free radicals, for example a chemical initiator. The radicals originate from initiator decomposition and attack the long chain polypropylene molecules by removing a hydrogen atom from a tertiary bonded CH group, causing chain scission (see Figure 3-1). Venting (devolatilization) is necessary to remove any monomer produced as well as any non-monomeric volatiles resulting from terminated initiator. The reaction is random with respect to the bond attacked, and since high molecular weight molecules have the most bonds these are preferentially degraded. This results in a reduction of the  $M_w$  and a narrowing of the MWD, as the high molecular weight tail degrades faster than the lower molecular weight species in the melt. The rate of reaction is very rapid. According to Suwanda et al. [19], the reaction is completed in 0.25 minutes at 220°C, with a peroxide initiator concentration of 0.04%. The amount of degradation is proportional to the initiator concentration. The presence of oxygen greatly increases the amount of degradation for a given concentration of initiator but causes undesirable discolouration and odours in the final product.

Several factors must be considered when choosing a source of free radicals. The major consideration is the initiator half-life at the reaction temperature. When using reactive extrusion to perform the degradation, care must be taken to select an initiator that is not so fast that it decomposes completely during melting (before it can be mixed with the polymer), or so slow that undecomposed initiator stays in the polymer to affect later processing or product life. Other factors include the initiator concentration range required for the desired range of product MWD and whether a master batch or an injected liquid will be used to introduce initiator into the process stream. Functionality is important, because multi-functional radicals can cause cross-linking instead of degradation. The type of radicals product. Finally, the initiator should not be so volatile as to cause handling problems and should cause no odours or colour changes in the final product.

Current technology for polypropylene visbreaking usually employs reactive extrusion and an organic peroxide initiator. The peroxides are either injected directly into the extruder or mixed with polypropylene to form a masterbatch of up to 5% peroxide by weight, which is then blended with straight polypropylene. Initiator concentrations are very low, as can be seen from Figure 3-2, and good concentration control is



Figure 3-2 Melt Flow Rate vs Initiator Concentration [18]

critical to assure a product with a uniform MWD. Unfortunately, due to sluggish extruder dynamics and the lack of suitable control sensors, closed loop control has never been effectively implemented for this process. Large variations in  $M_w$  within a single batch have been noted [20], leading to later processing problems. Fluctuating polymer properties upset the end-user's process, leading to waste material and poor finished product quality.

Several process models have been developed for single screw extruders to predict the effects of peroxide-promoted degradation on the MWD. Thermo-mechanical degradation is found to be negligible. The reaction goes to completion well before the polymer exits the extruder in both of the studies examined here. Suwanda et al. [21] developed a mechanistic model based on a simple reaction scheme, with a single unknown parameter, the initiator efficiency. This model predicts the entire MWD as a function of initiator concentration and shows the correct trends; a narrowing of the distribution and a chopping of the high molecular weight tail (see Figure 3-3). The



Figure 3-3 MWD of PP at various peroxide concentrations (from Suwanda et al. [19])

values of  $M_w$  and  $M_w/M_n$  calculated from these distributions are accurate to about 10% compared with data from size exclusion chromatography. Tzoganakis et al. [22] developed a model, based on a more complex reaction scheme, that predicts only the MWD moments ( $M_n$ ,  $M_w$  and  $M_z$ ). It shows about the same accuracy as the Suwanda model.

Twin screw extruders, such as the one used for this project, provide better mixing at lower shear rates than single screw extruders [23]. The models discussed above provide a rough estimate of  $M_w$  and MWD as long as the mean residence time in the extruder is sufficient for the reaction to go to completion and thermo-mechanical degradation due to excessive shearing is avoided. The models can be used to estimate the initiator concentration required to achieve a given degree of degradation.

# 3.2 Rheological Effects of Visbreaking

The ideal way to control modifications of the MWD of polypropylene would be to monitor the MWD itself. Size exclusion chromatography (SEC, also known as gel permeation chromatography, or GPC), where molecules are separated according to size, is usually used to determine the MWD within a sample. This technique is not suitable for on-line measurements, however, due to long measurement times and the need for elaborate sample preparation.

Since rheological properties depend strongly on the MWD of a polymer, they provide an extremely useful method of indirectly monitoring changes in the MWD during visbreaking. Viscosity functions generally vary in the same manner as  $M_w$ ; as  $M_w$  decreases, the viscosity at a given shear rate declines, and the viscosity curve becomes flatter. As can be seen in Figure 3-4, the sensitivity of viscosity to molecular weight



Figure 3-4 Viscosity curves of polypropylene with various  $M_w$  [18], with viscosity in Pas and shear rate in 1/s.

decreases as the shear rate increases. The zero shear viscosity,  $\eta_0$ , is a very strong function of  $M_w$ , with  $\eta_0 \alpha M_w^{3.5}$ . Elastic properties generally show a weaker dependence on  $M_w$ ; this relationship is quite difficult to measure because extremely low shear rates are required.

Polydispersity  $(M_w/M_n)$ , a measure of the breadth of the MWD, is generally opposite to  $M_w$  in its effect on rheological variables. Polypropylene tends to start shear thinning faster with increasing shear rate as  $M_w/M_n$  increases, but this dependence is weak compared to the effect of  $M_w$  on viscosity. Elastic variables, such as normal stress differences and the storage modulus G', are strongly dependent on  $M_w/M_n$ .

## 3.2.1 Determination of MWD from Dynamic Mechanical Analysis

Zeichner and Patel [24] have developed a technique for estimating the MWD of polypropylene from rheological measurements. Due to similarities in the MWD of polypropylene as polymerized with Zeigler-Natta catalysts and the statistics of random chain scission (both have approximately log normal distributions), only two parameters are needed to describe the distribution:  $M_w$  and  $M_w/M_n$ . All higher MWD moments can be calculated from these parameters, and all rheological properties can be correlated with them since they completely govern the MWD. Ziechner and Patel used dynamic mechanical analysis to determine  $\eta_0$  and a polydispersity index, which were then directly correlated to  $M_w$  and  $M_w/M_n$  as described in the following paragraphs.

Reduced variables were employed to superpose dynamic shear test data. According to the theory of linear viscoelasticity, in the low frequency range plotting G'' and  $\eta^*/\eta_0$  versus a reduced frequency,  $\omega_r = \eta_0 \omega$ , will superpose the curves, irrespective of M<sub>w</sub>, M<sub>w</sub>/M<sub>n</sub>, or temperature. G' will be superposed if M<sub>w</sub>/M<sub>n</sub> is held constant. Empirically, it was found that data for all variables are superposed over the entire frequency spectrum if M<sub>w</sub>/M<sub>n</sub> is constant. Variations in M<sub>w</sub>/M<sub>n</sub> cause G' and G'' curves to intersect each other at different values of the crossover modulus G<sub>c</sub> (G<sub>c</sub> = G' = G'' at the crossover point, and  $\omega_c$  is the crossover frequency). G<sub>c</sub> decreases with broadening MWD (see Figure 3-5). A "polydispersity index" (PDI) is defined such that



Figure 3-5 Effect of MWD on master curves (from Zeichner and Patel [24]).

$$PDI = \frac{10^6}{G_c \left(\frac{dynes}{cm^2}\right)}$$

A one-to-one correlation of  $M_w/M_n$  with PDI was established, allowing calculation of the breadth of the MWD from G<sub>c</sub> (see Figure 3-6).

Another property of the crossover modulus is that it occurs at a reduced frequency  $\omega_{rc}$  that depends on PDI only, giving the correlation:

$$\ln(\omega_{m}) = 14.73 - 0.237 \ln(PDI)$$

Knowing the crossover frequency,  $\omega_c$ , the zero shear viscosity can be calculated ( $\eta_0 = \omega_{rc}/\omega_c$ , in Poise) to within 5% without taking any low frequency or low shear rate measurements.  $\eta_0$  is, as mentioned before, a strong function of  $M_w$ ; Zeichner and Patel



Figure 3-6 Correlation of PDI with  $M_w/M_n$  (from Zeichner and Patel, [24]). have included polydispersity in their viscosity correlation as well, giving:

$$\ln(\eta_0[Poise]) = -35.4 + 3.61 \ln(M_w) + 0.84 \ln(\frac{M_w}{M_n})$$

After rearrangement, and using the polydispersity calculated earlier from  $G_c$ , Eqn (3-3) can be used to determine  $M_w$ . The correlation is valid for  $\eta_0$  in Poise at 200°C.

## 3.2.2 Use of the Melt Flow Rate

Another rheological measurement widely used in industry is the melt flow rate (MFR). While not a well defined rheological property of a polymer, it is widely used to compare various lots of the same polymer, as well as to characterize different grades of the same type of polymer. In the melt flow test, a weighted piston extrudes molten polymer through a short capillary tube. The amount extruded during 10 minutes is collected and weighed. This quantity is defined as the "melt flow rate" (MFR), which has units of grams/10 min. Different polymers make use of different standard piston

weights and test temperatures, so the MFR is not a good method of comparing different polymers. The standard test values for polypropylene are 2.16 kg and 230°C (ASTM D1238-65T).

The MFR value is often the quality control specification used for polypropylene, so it is an obvious candidate for use as a control variable. To accomplish this, a process rheometer can be used to approximate the MFR standard test conditions. Both the force on the MFR piston and the geometry of the testing apparatus are known, and the apparent shear stress,  $\sigma_{app}$ , is a constant. The apparent shear rate,  $\dot{\gamma}_{app}$ , can be calculated from the MFR value. Ideally, a rheometer would have to work at constant stress and measure  $\dot{\gamma}_{app}$ to correctly simulate the MFI apparatus. Most process rheometers, however, impose a shear rate and measure the resulting shear stress, so that a more complex strategy is required. Two approaches are possible: using viscosity at a shear rate chosen to approximate the MFR test conditions, or correlating the MFI with dynamic shear measurements.

Curry and Jackson [25] used a Goettfert Bypass Rheograph (an on-line capillary rheometer) mounted on the end of a twin-screw extruder to approximate the MFR test conditions for control purposes. The shear rate chosen for the rheometer was the rate associated with the desired setpoint MFR, so that the value of the apparent shear stress,  $\sigma_{app}$ , felt by polymer at the setpoint is the same as in the MFR apparatus. The shear viscosity can then be correlated with the MFR for that region, giving better results the closer the process MFR is to the setpoint.

Fritz and Stöhrer [10] used a Rheometrics On-line Rheometer (section 1.2) to measure the complex viscosity,  $\eta^*$ , at a single frequency  $\omega_m$ . The Cox-Merz relationship,  $\eta^*(\omega_m) = \eta(\dot{\gamma})$  for  $\omega_m = \dot{\gamma}$ , was employed to select an optimal measuring frequency for  $\eta^*$  based on an  $\dot{\gamma}_{app}$  value calculated from the setpoint MFR. The MFR was correlated with  $\eta^*$  for the region around the setpoint as follows:

$$\frac{MFR_{act}}{MFR_{sp}} = \left(\frac{\eta^*(\omega_m)_{act}}{\eta^*(\omega_m)_{sp}}\right)^{-1.8}$$

where the subscript "act" refers to actual process measurement and "sp" refers to the value obtained at the process setpoint. This correlation is good when  $\log(MFR_{act}/MFR_{sp})$  is between  $\pm 0.1$ , or for a  $\pm 25\%$  range about MFR<sub>sp</sub>.

# 3.3 Process Identification and Control Background

Polypropylene visbreaking is perhaps the most studied reactive extrusion process. The product rheology is very sensitive to the molecular weight distribution, which in turn is sensitive to the amount of free radical initiator introduced to the process. The system can be easily controlled to a rheological setpoint (such as viscosity) by varying the initiator concentration in the feed stream. Also, the visbreaking reaction is fast enough at process temperatures, relative to the polymer residence time in the extruder, that the reaction kinetics do not have to be taken into account. A widely used commodity polymer, there is considerable interest and support from industry for studies involving polypropylene, and the visbreaking process itself is straightforward to implement.

It was for these reasons that this system was chosen for this project. With a well understood process, the major effort could be concentrated on rheometer development and process control. Many other groups have studied closed loop control of the visbreaking process, achieving varying levels of performance. This allows the experimental observations, including the effectiveness of the in-line viscosity sensor, to be compared with those of other groups using commercial rheometers. Several of these previous studies are described in the following paragraphs.

Fritz and Stöhrer [10] used a Rheometrics On-line Rheometer to make complex viscosity measurements, which were correlated with an MFR (as explained in section 3.2.2). Two gravimetric feeders were used to feed polypropylene and a peroxide masterbatch to a Werner and Pfleiderer ZSK-30 twin-screw extruder. Process identification experiments showed a dead time of  $t_d=180$  s and a first order process time constant of  $\tau_p=156$  s when lowering the MFR and  $\tau_p=192$  s when raising the MFR. Employing a straightforward PI controller, step changes in the MFR setpoint required

about 780 seconds to settle, while load disturbances to the system required about 1500 s to recover.

Curry and Jackson [25] also used a ZSK-30 fed by two gravimetric feeders, with a Goettfert Bypass Rheograph providing a simulated MFR signal (section 3.2.2). Again, a masterbatch was used to control the peroxide concentration in the process, and control was achieved using a PI controller with gain scheduling. Open loop results gave  $t_d=288$  s and  $\tau_P=240$  s, with process settling times of 500 to 600 s for steps in the controller MFR setpoint with the control loop closed.

Pabedinskas et al. [26] used a single-screw extruder with peroxide injected into the feed throat. The control variable employed was the pressure drop through the die, which was correlated with values of  $M_w$ . This was, in effect, an "in-line" rheological measurement, but various sources of pressure fluctuations, such as feed rate variations, had to be considered as well. They found their system had a dead time  $t_d=160$  s and a first order time constant  $\tau_p$  in the range of 95 to 165 s. Using a Smith-Predictor scheme with gain scheduling, they achieved process response times of about 720 s for a step change in the die pressure setpoint. This is similar to the value Fritz reported, even though here a model-based controller was employed; noise in the pressure signal may have limited the gain settings possible for the controller.

Dumoulin et al. [27] also used a single-screw extruder and injected their peroxide initiator. A Rheometrics Melt Flow Monitor (section 1.2) was used to measure the viscosity at 100 1/s, with  $t_d=240$  s and  $\tau_p$  varying from 100 to 192 s. The high shear rate was used to avoid sampling delay in the rheometer; values of  $t_d$  and  $\tau_p$  at 10 1/s were more than double those for 100 1/s. Experiments with the rheometer in the constant stress mode had widely varying dead times due to the changing flow rates through the rheometer and so were not used in the control studies. A simple PI controller was used to control the peroxide flow rate; rise times of 400 s with 1350 s settling times were achieved for setpoint changes, while load disturbances took 600 s to return to the setpoint and 1800 s for oscillations to die out completely.

The most direct comparisons with the present work can be made with the first two studies, since the process equipment used was identical to the equipment used in this project with the obvious exception of the rheometers. Curry and Jackson reported the best control results, even though they had the longest time constants in their identification model. This is likely due to good controller tuning and low noise in the process measurement. The single-screw experiments have slightly longer time parameters, because the single screw-extruders tend to have broader residence time distributions than twin-screw units. However, they still supply valuable information on the process dynamics and insights into the operation of various process rheometers.

## 3.4 Base Polypropylene Characterization

The resin used in this project was supplied by Himont Canada. A single, large shipment (close to 3 tonnes) of Profax 6631 (Batch #11564-B55), a polypropylene resin in pellet form with MFR  $\approx 2$  g/10 min (ASTM D1238-65T), was used. A single batch was used to ensure consistency throughout the various process identification and control



Figure 3-7 Storage and loss moduli, complex viscosity and shear viscosity measurements for Profax 6631 polypropylene at 200 °C.

experiments. Figure 3-7 shows storage and loss moduli, complex viscosity and shear viscosity over the region of interest. This polypropylene does not follow the Cox-Merz

rule,  $\eta(\gamma) = \eta^*(\omega)$ ; in fact the complex viscosity is roughly twice that of the shear viscosity in the region of measurement.

A stabilizer had been added to the polymer by Himont to protect it from degradation during shipment and storage. The stabilizer reduces the amount of degradation occurring in the process by reacting with a fixed number of the peroxide radicals. Assuming the stabilizer concentration to be approximately uniform in all of the pellets, the amount of peroxide necessary to achieve a specified amount of degradation is thus increased by a constant amount. This effect of the stabilizer may be a source of the nonlinearity in the dependence of the process gain on viscosity (Section 7.2.1). At low peroxide concentrations, a large percentage of the peroxide will react with the stabilizer; at higher concentrations, the relative fraction of the peroxide consumed by the stabilizer will decrease, changing the process gain. At a low concentration, for example, if half of the peroxide in the feed stream is consumed by stabilizer, then doubling the peroxide in the feed stream will triple the amount of peroxide actually degrading the polymer, since the amount of peroxide that reacts with the stabilizer is now only a quarter of the total instead of one half. Doubling the feed concentration again results in an increase of peroxide reacting with the polymer of 2.33 times, a reduced gain compared with the initial step. This reduction in gain continues as the relative fraction of peroxide reacted by stabilizer becomes smaller; when it becomes negligible, doubling the feed stream concentration will double the peroxide to the polymer. Bag to bag variations in the polymer stabilizer concentration are also thought to account for slight offsets in the measured viscosity when starting new bags of polymer.

Zeichner and Patel's correlations (section 3.2.1) were employed to estimate the effects of the visbreaking process on the MWD of the polypropylene. The 5% uncertainty in the  $\eta_0$  estimation works out to less than 2% uncertainty in the M<sub>w</sub> for this range of molecular weights. Measurements before and after the polymer was extruded were made, as well as at low and high peroxide concentrations (see Table 3-1). The 95% confidence interval for the M<sub>w</sub> estimates was less than 4000, while the confidence interval for M<sub>w</sub>/M<sub>n</sub> estimates was 0.05.

Peroxide Conc	G <sub>c</sub>	ω	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
0 ppm (before)	28700	16	3.40x10⁵	3.8
0 ppm (after)	30100	22	3.21x10 <sup>5</sup>	3.7
100 ppm	34600	31	2.69x10⁵	3.2
400 ppm	39600	97	2.06x10 <sup>5</sup>	2.8

**Table 3-1** Estimates of  $M_w$  and  $M_w/M_n$  for Profax 6631 polypropylene before and after extrusion, and at low and high peroxide concentrations. Typical crossover moduli and frequencies are included, in Pa and rad/s respectively.

The samples for the unprocessed MWD estimates were taken from six bags of polymer distributed throughout the batch. The results from each bag were similar, suggesting that the MWD was constant, to within the accuracy of Zeichner and Patel's correlations, throughout the entire batch. The drop in  $M_w$  after passing through the extruder with no peroxide shows the effects of thermo-mechanical degradation. This is negligible, however, compared to the decrease in  $M_w$  caused by peroxide-promoted degradation at concentrations of 100 and 400 ppm. The polydispersity of the polymer,  $M_w/M_n$ , is also significantly reduced, indicating the expected narrowing of the MWD.

## 3.5 Peroxide Masterbatch Preparation

A dialkyl peroxide, 2,5-dimethyl-2,5(t-butylperoxy)hexane (tradename Lupersol 101)<sup>1</sup>, was selected as the initiator for the visbreaking process. This peroxide is mentioned in many publications on the visbreaking process [10,21,25] and is widely used in industry for this purpose. According to the product literature, the half life of the peroxide is 90 s at 170°C, about 30 s at 180°C and is less than 5 s at 200°C. Thus, this material does not decompose immediately upon introduction into the extruder. It blends with the polymer melt before rapid decomposition, which commences when the polymer

<sup>&</sup>lt;sup>1</sup> see Appendix D for material safety data sheet

temperature reaches the 190 to 200°C range. At temperatures over 200°C, the half life of the peroxide is close to zero, ensuring that all the peroxide has decomposed before the polymer exits the extruder.

Preparing the masterbatch involved coating polymer pellets evenly with a small amount of a low viscosity fluid. To facilitate this, the peroxide was diluted with an ECS grade of light paraffin oil, with which the peroxide was completely miscible. This oil has a flash point of 175°C, and it was assumed that most of the oil would flash after the reaction in the devolatilization zone of the extruder (where the temperature is 190°C to 200°C). In fact, Suwanda et al. used this method of diluting peroxide (20% peroxide, 80% paraffin oil) for their degradation experiments in a single screw extruder with no devolatilization and found the addition of small quantities of paraffin oil (up to 400 ppm) to have no noticeable effect on their process [28]. Therefore, even if some paraffin oil stays in the polymer, it is assumed to have no effect or the viscosity measurements.

The Lupersol 101 was diluted to a 20% solution in the paraffin oil before dispersion on the polypropylene pellets. Two masterbatch concentrations were used; masterbatch "A" at 1000 ppm peroxide, and masterbatch "B" at 500 ppm. The pellets from batch A were damp and slightly sticky. When batch B was prepared, the same peroxide dilution but half the total amount of liquid was used.

Both masterbatches were prepared at the Himont plant in Varennes, Quebec, using two low-intensity mixers. The peroxide becomes unstable and decomposes at temperatures over 86°C, so care was taken to ensure that the polymer did not heat up during mixing. A Littleford blender was used initially to disperse the peroxide solution on the pellets. This blender has wedge-tipped mixing arms that rotate at approximately 50 rpm, but it can hold only 25 kg in a single charge. Peroxide was added in two doses, with 2 minutes of mixing between them and 5 minutes after the final dose. Once the peroxide was dispersed on the polymer, the 25 kg batches were all loaded into a large ribbon blender and mixed for 15 to 20 minutes, to ensure overall batch uniformity (The total batch sizes were around 200 kg). From this mixer, the masterbatches were loaded into plastic-lined and sealed 25 kg barrels for shipment. As long as the barrels remained sealed, the masterbatches had sufficient shelf life for the experiments in this work (several months - the assay on the peroxide as received was guaranteed by the manufactured for one year).

۰.

# CHAPTER 4 EXPERIMENTAL APPARATUS

Much of the equipment used for this project was new and had to be installed before any experiments could be performed. This included a new twin-screw extruder with gravimetric feeders and a vacuum devolatilization system. A modular control





system was used for temperature, extruder drive and feeder control, along with pressure monitoring, sequence logic programming and process alarms. This system was linked through a serial communications line to a PC compatible computer, which provided data acquisition and supervisory setpoint control functions for the extruder. The stress, strain rate and pressure signals from the rheometer were fed directly to the PC. Figure 4-1 is a schematic showing the functional relationship between the various system components. The PC was employed for closed loop viscosity control, using the viscosity from the rheometer to calculate changes in the peroxide

implementing these changes through the MACO 8000. Details on the rheometer can be found in Chapter 2.

# 4.1 Werner and Pfleiderer Twin Screw Extruder

The polypropylene visbreaking process was carried out in a Werner and Pfleiderer ZSK-30 co-rotating, intermeshing, twin-screw extruder. A twin-screw extruder was selected over a single-screw design for several reasons. It is capable of providing more intense mixing than a single-screw unit, ensuring a more uniform distribution of the peroxide initiator throughout the melt and providing better devolatilization. Also, the screw speed, which governs the intensity of the mixing, and the polymer throughput rate are independent in a twin-screw machine. This allows better control of the residence time and the residence time distribution, and makes the twin-screw unit much more flexible. This machine is becoming very popular in the plastics industry and is the machine of choice for most compounding and reactive extrusion processes, where good control of the degree of mixing is required.

The barrel, with an L/D ratio of 27, was divided into four temperature control zones, each with ON/OFF water cooling. A downstream feed port (not used in this project) and a devolatilization vent were also included. A 250 W vacuum pump was connected to the devolatilization vent. The extruder was equipped with a 15 HP electric motor, capable of driving the screws at speeds up to 500 rpm.

The screw design for the two 30 mm screws was recommended by J. Curry of Werner and Pfleiderer. It is similar to the screw design that he employed in similar polypropylene visbreaking extrusion experiments [25]. The screw configuration, shown in Appendix D, can be divided into four sections, each separated from the others by a melt seal. Starve fed, twin-screw extruders run with the screw flights only partially filled along most of their length. In order to prevent the flow of gasses along the screw, reverse flighted elements (left handed flights) are inserted at intervals. They push back against the flow of the melt, filling the extruder cross-section to form a seal. The screw sections are as follows:

- Feeding and melting section In this section, polymer pellets are melted and reactants blended. Kneading blocks furnish high shear mixing, and the viscous heat generated helps to melt the polymer.
- Reaction section A melt seal is formed at both ends of this section to provide a closed environment for the reaction. This prevents the release of gases to the atmosphere through the feed ports.
- 3) Devolatilization section The melt seal at the end of the reaction section and the start of the pumping section seal this section so that a vacuum can be drawn through the devolatilization vent. Off-gases, which come through the reaction section melt seal and form bubbles in the polymer, and traces of volatile reaction by-products and remaining reactants are removed by the vacuum.
- 4) Pumping section This section is the only portion of the screw (excluding the seals) that runs 100% full of polymer. It provides the pumping pressure (this machine is rated to 30 MPa) necessary to push the polymer out of the extruder and through a die.

Thus, the ZSK-30 is a good choice for the visbreaking process; powerful and versatile enough to handle the flow rates and mixing required by the process, but small enough to be practical for a laboratory scale process.

## 4.2 The MACO 8000 Control System

The MACO 8000, manufactured by the Barber Colman Co., is a modular distributed control system. The configuration used here consisted of six modules: two heat/cool modules for temperature control of the extruder and the rheometer, a drive module for extruder drive and feeder control, a pressure module for monitoring process pressures, a sequence module to provide sequence logic control, and an "insta-set" module to handle inter-module communications, external computer links and the MACO touch-sensitive cathode ray tube (CRT). Each module has two microprocessors: one to

perform control functions and one to link with the communications bus controlled by the insta-set module.

The MACO 8000 has two main functions. The first is to provide control and safety features for the extruder drive, the gravimetric feeders, and all temperature zones in the extruder and the rheometer. The second function is to act as a data acquisition system for the process control computer. The MACODRV communication subroutines (see section 4.4) allow the control computer to receive data from and send setpoints to the MACO 8000 through an RS-232 serial line.

A touch sensitive CRT is provided to enable the operator to adjust setpoints, monitor process values and control the system. The MACO 8000 CRT comes with system screens designed for the control of extruder processes. While they contain all of the necessary setpoints and controls, they also include calibration, configuration, tuning and trouble-shooting routines that are rarely used. The essential functions are spread out over many screens, and much moving between screens is necessary to operate the system. To eliminate this inconvenience, monitor screens containing the most used readouts, setpoints and controls were added to the system screens. Three main screens, the Process Enables Screen, the Process Temperature Monitor and the Process Drive Monitor, are sufficient to run the extruder under most circumstances. Several auxiliary screens containing additional functions and help information were also added. The MACO 8000 Setup and Operations Manual, the Screen Editor Manual and the Sequence Logic Programming Manual (Barber Colman, 1989) explain in detail the standard system screens, while the MACO 8000 Operator's Guide (see Appendix E) describes the custom screens.

The sequence logic program, which resides in the MACO 8000 sequence module, is the software that connects buttons and switches on the touch-sensitive CRT to the hardware that performs the control activities. It also provides the means by which safety interlocks (such as the interlock which disables the extruder motor until the process is up to temperature), process alarms (such as motor over-torque) and the emergency stop button are installed on the system. PC based editors and compilers from Barber-Colman were used to edit and compile the logic program and the control screens, which were then
downloaded to the MACO through the serial communications line. The major features of the logic program are also covered in the MACO 8000 Operator's Guide.

# 4.3 Gravimetric Feeders

The manipulated variable of choice for the visbreaking process was the weight percent of the peroxide initiator in the feed stream. Two feed streams, one a masterbatch mixture of polypropylene and peroxide and the other straight polypropylene, were starve fed into the extruder. A masterbatch system was chosen over direct injection of the peroxide for two reasons. The low concentration of initiator required in the process would have called for extremely low peroxide injection flow rates (on the order of 2 to 5 g/h), making proper mixing with the polymer before reaction difficult. The safety considerations involved in injecting an explosively unstable compound into a high temperature polymer melt were also a major factor in the decision to use a masterbatch.

Two Control and Metering twin screw gravimetric feeders were purchased and installed to meter these streams. Good control of the feed rate (to within  $\pm 1\%$  of the full scale range) was necessary to reduce noise in the peroxide concentration, which could later manifest itself as noise in the viscosity signal. A study by Curry et al. [29] found that random errors in the feed rate are effectively damped by a twin-screw extruder, but that systematic errors, such as the feeder cycling about a setpoint, are only slightly damped. Calibrations were performed by collecting and weighing the material fed over a certain period of time to ensure that the feeders performed as specified. No systematic errors were detected.

Two types of screw were used in the feeders. Feeder 1, used to feed the straight polypropylene, had screws designed for feed rates between 3 and 30 kg/h. Feeder 2, which metered the masterbatch, had screws designed for rates between 2 and 20 kg/h. At rates below the recommended range, the feeders were not completely stable, although performance was acceptable down to approximately 0.5 kg/h below the suggested minimum. It was this limit, along with the peroxide concentration in the masterbatch,

that governed the minimum peroxide concentration setpoint above zero (pure polypropylene) achievable in the feed stream.

The feeder design has the material hopper, feed throat, drive motor and gearbox all mounted on a balance connected to a digital load cell. The loss in weight as the feeder empties is monitored by a computer (a CONGRAV controller unit manufactured by Brabender) that adjusts the feeder screw speed to give the desired mass flow rate. The CONGRAV uses a PID control algorithm, with all parameters adjustable by an operator; the feeders were tuned by trial and error over a considerable period of time to get a critically damped response to changes in the feeder setpoints. With this tuning, the feeders were observed to settle to their new rates in approximately 15 seconds. The CONGRAV units receive feed rate setpoints in the form of a 0-10 V signal from the MACO 8000 drive module. The MACO 8000 is also capable of turning the feeders on and off remotely.

## 4.4 MACO 8000 - PC Communications

Two sources of information were used for data acquisition. First, the Data Translation DT-2801-A board mounted in the PC-compatible control computer converted analog signals to a digital form for the PC (Section 2.5). Secondly, the PC was connected through a serial communications line (null modem cable, 9600 baud, 8 bits/byte, no parity, 1 stop bit) to the MACO 8000 insta-set module. To facilitate communications programming, a collection of subroutines were written in QuickBASIC (version 4.5, from Microsoft) and added to the "Quick Library", so that they could be used as if they were internal BASIC commands. These routines were used to send and request information from any MACO 8000 module, giving the PC further data acquisition capabilities. Any variable the MACO 8000 monitored was available to the PC. Any setpoint in the MACO 8000 could be changed using the routines, giving the PC supervisory setpoint control. Also, the PC could activate any of the panel relays (touch sensitive areas on the CRT) that appeared on the MACO control screens, giving the PC

limited sequence logic control. These features were used by programs run on the PC to adjust the feeder setpoints and control the visbreaking process.

While the serial line between the PC and the MACO 8000 is open (ready to transmit data), the communications link between the MACO 8000 modules is suspended. This does not affect the control functions of the modules, but inter-module communications such as alarms or refreshing the information on the MACO 8000 CRT, are interrupted. It is therefore necessary to keep the communications link to the MACO 8000 open for short periods of time only. MACO.OPEN and MACO.CLOSE commands are included in the subroutines. Generally, the time required to open the serial line, read or write a list of variables, and then close the line was less than a second, and no problems were encountered. If the line was held open for a substantial length of time (20 to 30 s), a PC-timeout error would occur in the MACO 8000.

Note that in order to access the MACO 8000 with an external computer, the remote access relays found on the "RS-232" screen must be energized. The level of access could be set to full or to read-only, which allowed data acquisition only.

For a full listing of the routines and their functions, see the manual; "The MACODRV Version 2.1 PC - MACO 8000 Communications Subroutines" (see Appendix E).

## **CHAPTER 5**

# DYNAMIC MECHANICAL ANALYSIS USING COMPLEX WAVEFORMS

#### 5.1 Introduction

The visbreaking process modifies the molecular weight distribution (MWD) of polypropylene. The cross-over modulus and frequency ( $G_C$  and  $\omega_C$ ) of the storage and loss moduli (G' and G") curves have been correlated directly with the molecular weight average ( $M_w$ ) and the polydispersity ( $M_w/M_N$ )[24,30]. Monitoring these variables would allow control of the process to be based on the MWD.

A considerable number of points in the vicinity of the cross-over point are needed to accurately determine the cross-over values. To measure these points one at a time, however, would require very long rheometer measurement times, eliminating the in-line rheometer's advantage of a quick response. A method is needed to quickly determine a large number of points over a range of frequencies. A complex waveform consisting of the superposition of a number of frequencies rather than a sinusoid gives results for all these frequencies simultaneously.

A method of performing multi-frequency measurements was developed using a Rheometrics Dynamic Analyzer (RDA II) and then employed to perform dynamic mechanical analysis (DMA) using the in-line rheometer.

### 5.1.1 Storage and Loss Moduli as Complex Variables

Small amplitude oscillatory shear is a widely used method of determining the linear viscoelastic properties of materials. In the classical version of the technique the material is subjected to a sinusoidal shear strain of amplitude  $\gamma_0$  and frequency  $\omega$ , such that the shear strain is:

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{5-1}$$

If the response is linear, i.e., if the strain amplitude is sufficiently small, the resulting shear stress will also be a sinusoid:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$$
 (5-2)

where  $\delta$  is the phase angle or mechanical loss angle and  $\sigma_0$  is the stress amplitude. Furthermore,  $\sigma_0$  at a given frequency is proportional to  $\gamma_0$ .

While the linear viscoelastic behaviour can be described in terms of the amplitude ratio or "dynamic modulus",  $G_d \equiv \sigma_0 / \gamma_0$ , and the phase angle,  $\delta$ , as functions of frequency, it is customary to rewrite Eqn (5-2) using a trigonometric identity as follows:

$$\sigma(t) = \gamma_0 [G' \sin(\omega t) + G'' \cos(\omega t)]$$
(5-3)

where  $G'(\omega)$  is the storage modulus and  $G''(\omega)$  is the loss modulus, which are functions of frequency. The values of these functions at a given frequency can be calculated from the amplitude ratio and phase shift using:

$$G' = G_d \cos(\delta)$$

$$G'' = G_a \sin(\delta)$$
(5-4)

The complex modulus,  $G^*(\omega)$ , is a complex-valued function whose real and imaginary parts are the storage and loss moduli, respectively:

$$G^*(\omega) = G'(\omega) + jG''(\omega)$$
(5-5)

where  $j \equiv (-1)^{1/4}$ . The dynamic modulus,  $G_d$ , is equal to the magnitude of the complex modulus,  $|G^*|$ . Values of  $G^*(\omega)$  can be calculated directly from experimental data, as explained in section 5.2.

The standard method of measuring  $G'(\omega)$  and  $G''(\omega)$  is to perform sinusoidal shear experiments at a series of frequencies and to construct the response curve one point at a time. This is not an efficient use of time or information, as one must sample an entire waveform to get a single datum. However, a complex strain history, with a broad frequency content, provides information about the response over a range of frequencies in a single measurement. The discrete Fourier transform (DFT) can be used to analyze the complicated stress signal to yield values of the storage and loss moduli at a number of frequencies [31]. In this way, the shape of the response curves can be established very quickly.

## 5.2 Frequency Analysis of Complex Waveforms

The discrete Fourier transform (DFT) separates a periodic discrete time series into its Fourier components. In other words, it calculates the amplitudes of the sine and cosine waves at each of the discrete frequencies that make up the Fourier series representation of the discrete signal. For the Fourier series

$$f(t) = \sum_{i=0}^{N-1} a_i \cos(\omega_i t) + b_i \sin(\omega_i t)$$
(5-6)

the DFT yields the coefficients  $a_i$  and  $b_i$ . The DFT can be used to analyze the stress signals generated by a complex strain history to find the amplitude of the stress response for any particular frequency component.

To understand how the analysis works, consider a sinusoidal strain at a frequency  $\omega_0$ . The strain and resulting stress are given by equations (5-1) and (5-2), which are plotted in Figure 5-1. As mentioned at the beginning of this chapter, the quantities arising directly from the experimental data are  $G_d$  and  $\delta$ , and this analysis will be based on these. Approaching the analysis from the frequency viewpoint, both the stress and the strain are transformed into the frequency domain:

$$\gamma^{*}(\omega) = DFT[\gamma(t)]$$

$$\sigma^{*}(\omega) = DFT[\sigma(t)]$$
(5-7)

The transform produces complex valued functions of frequency that are zero at every frequency except  $\omega_0$ :



Figure 5-1 - Sinusoidal Strain and Resulting Stress

$$|\sigma^*(\omega_0)| = \frac{1}{2}\sigma_0 \qquad |\gamma^*(\omega_0)| = \frac{1}{2}\gamma_0$$

The quantities  $G_d$  and  $\delta$  are then calculated as follows:

$$G_{d} = |G^{*}(\omega_{0})| = \frac{|\sigma^{*}(\omega_{0})|}{|\gamma^{*}(\omega_{0})|}$$

$$\delta = phase[\sigma^{*}(\omega_{0})] - phase[\gamma^{*}(\omega_{0})]$$
(5-8)

The operations of equations (5-8)a and b are equivalent to the complex division of  $\sigma^*(\omega_0)$  by  $\gamma^*(\omega_0)$ .  $G^*(\omega_0)$ , containing both amplitude and phase information, can be determined directly from the frequency domain data; all other functions can then be obtained from  $G^*(\omega_0)$ :

$$G^{*}(\omega_{0}) \equiv \frac{\sigma^{*}(\omega_{0})}{\gamma^{*}(\omega_{0})}$$

$$\delta(\omega_{0}) = phase[G^{*}(\omega_{0})]$$

$$G'(\omega_{0}) = real[G^{*}(\omega_{0})]$$

$$G''(\omega_{0}) = imag[G^{*}(\omega_{0})]$$
(5-9)

Consider next a strain history composed of two superposed sinusoids of frequencies  $\omega_1$  and  $\omega_2$  (see Figure 5-2).

 $\gamma(t) = \gamma_1 \sin(\omega_1 t) + \gamma_2 \sin(\omega_2 t)$ 

(e) 
$$1500$$
  
 $1000$   
 $500$   
 $-500$   
 $-500$   
 $-1000$   
 $-1500$   
 $-1000$   
 $-1500$   
 $-1000$   
 $-1500$   
 $-1000$   
 $-1000$   
 $-1000$   
 $-1000$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   
 $-100$   

$$\sigma(t) = \sigma_1 \sin(\omega_1 t + \delta_1) + \sigma_2 \sin(\omega_2 t + \delta_2)$$

Figure 5-2 - Strain composed of two superposed sine waves and resulting stress response

One feature of linear viscoelasticity is that the stress in the material at any time, t, is the sum of the stresses resulting from each of the individual strains that the material has

experienced at past times. This implies that the stress resulting from a composite strain waveform is simply the sum of the stresses arising from the individual components of the strain. In this case, the stress due to the superposed sinusoids is the sum of the responses the individual sinusoids would have caused alone. Since a time-based method of analysis would be very difficult to use, a frequency-based analysis is preferred.

Now there are two frequencies,  $\omega_1$  and  $\omega_2$ , at which the transformed strain and stress functions have non-zero magnitudes. The analysis performed at  $\omega_0$  for the single sinusoid can be performed at  $\omega_1$  and  $\omega_2$  for the composite waveform. The stress and strain signals are thus transformed into the frequency domain, giving:

$$\begin{aligned} |\gamma^*(\omega_1)| &= \frac{1}{2}\gamma_1 \qquad |\gamma^*(\omega_2)| &= \frac{1}{2}\gamma_2 \\ |\sigma^*(\omega_1)| &= \frac{1}{2}\sigma_1 \qquad |\sigma^*(\omega_2)| &= \frac{1}{2}\sigma_2 \\ G^*(\omega_1) &= \frac{\sigma^*(\omega_1)}{\gamma^*(\omega_1)} \qquad G^*(\omega_2) &= \frac{\sigma^*(\omega_2)}{\gamma^*(\omega_2)} \end{aligned}$$

Thus, viscoelasticity information at two frequencies is obtained.

This technique can be expanded to include n sine waves at n different frequencies, using frequency analysis techniques to calculate  $G^*(\omega)$ . Note that  $\omega_i = k \cdot \omega_0$ , where k is an integer, i.e., all the higher frequencies must be integral multiples of the lowest, fundamental frequency to ensure that all frequencies are harmonically related. Any periodic waveform can be represented by a Fourier series (sum of sine and cosine waveforms) and can, in principle, be used as a strain history.

There are, however, some limitations on the choice of the strain waveform. The maximum amplitude of the composite strain must not exceed the linear viscoelastic limit of the material being tested. At the same time, each stress component must have an amplitude large enough to be sensed by the stress or force transducer used in the rheometer. The strain amplitudes should be chosen so that the resulting stress amplitudes are all about the same. Thus, high-frequency components should usually have smaller

24

amplitudes than those at low frequency, since they cause larger stress responses. Also, they are repeated many times during the course of the measurement, allowing the DFT to average the signal over several cycles and thus improve the signal to noise ratio.

Notice that in the analysis it is the actual measured strain that must be used rather than the command strain signal sent to the rheometer drive controller. These two signals are often not the same, particularly for strain waveforms with high frequency components. The drive motor, for example, can act as a filter, reducing or even eliminating high frequency components that are beyond its response range. The drive response at high frequencies is one of the limits of any testing system.

#### 5.3 Properties of the Discrete Fourier Transform

The discrete Fourier transform (DFT) works with discrete rather than continuous signals. It transforms a discrete time domain set of data to a discrete, complex-valued, frequency-domain series and is defined as follows:

$$X(k) = \frac{1}{N} \sum_{n=0}^{N-1} x(n) e^{\frac{-j2\pi kn}{N}}$$
(5-10)

where x is the time based signal, X is the transformed signal, N is the number of data points,  $j = \sqrt{-1}$ , and k is the kth element in X. Using Euler's identity, X can also be expressed as

$$X(k) = \frac{1}{N} \sum_{n=0}^{N-1} x(n) \left[ \cos\left(\frac{2\pi kn}{N}\right) - j \sin\left(\frac{2\pi kn}{N}\right) \right]$$
(5-11)

The calculation of the DFT is easily accomplished using a computer by simply taking the sum of the terms shown in equations (5-10) or (5-11). However, this is usually very time consuming, even on a fast computer. A number of algorithms, called fast Fourier transforms (FFT), have been developed that greatly speed the calculation [32]. To calculate the DFT, the number of mathematical operations required is

proportional to  $N^2$  whereas the FFT algorithms require only  $N \cdot \log_2(N)$  operations which is much less than  $N^2$  when N is large. A limitation of the FFT is that it generally requires the data series to be a power of two in length (i.e. to have 2, 4, 8, 16, 32, ... elements).

Fourier analysis is based on the Fourier series representations of a function,

$$x(t) = a_0 + \sum_{i=1}^{\infty} [a_i \cos(i\omega_0 t) + b_i \sin(i\omega_0 t)]$$
 (5-12)

where  $\omega_0 = 2\pi/T$ , T = the period of the waveform = 1/F, and F = the fundamental frequency. Note that an infinite series is used to represent continuous functions, while a finite series is used for discrete functions (such as sampled data). Fourier analysis assumes that the waveform being studied is periodic, i.e., that x(t)=x(t+T), where T is the period of the waveform, and that it extends in time from negative to positive infinity.

Of course, this assumption is not valid for physical systems, since these must have specific starting and ending times. Start-up transients in the input strain and the stress



Figure 5-3 - Start-up transients in a dynamic measurement using a multi-sinusoid composite waveform

response will cause aperiodicity in the measured signals at the start of a test. In Figure 5-3, three cycles of a complex strain history are shown, along with the resulting stress response. The first three peaks of the initial cycle differ considerably from the corresponding peaks in the following cycles, due to start-up transients. This transient response becomes negligible about halfway through the first cycle, so that by the second cycle a periodic signal is achieved. Repeating the waveform until any transients have become negligible before sampling data is sufficient to ensure that the assumption of periodicity is valid. If the waveform has a very long period, only part of it may need to be repeated. As a rule of thumb, the strain should be applied for a length of time greater than the longest relaxation time of the material being tested before recording any data points. Stress relaxation experiments (monitoring the stress response to a step in strain) can be used to get an estimate of the longest relaxation time.

Another important property of the DFT is that it is linear. A component added in the time domain is also added in the frequency domain. This allows the construction of a waveform with a desired frequency spectrum by adding together appropriate waveforms in the time domain. Each waveform adds its own components until the desired frequency spectrum is achieved.

## 5.3.1 Aliasing

In comparing discrete and continuous data, a factor of central importance is the sampling rate. If this rate is higher than necessary, surplus data will be collected, resulting in long calculation times and excessive data storage requirements. If the sampling rate is too low, not enough information is collected and aliasing occurs.

The Nyquist sampling theory (known also as Shannon's theory) states that the sampling frequency,  $f_s$ , must be at least twice that of the highest frequency component in the signal being sampled. Conversely, the Nyquist frequency,  $f_{Nyq}$ , is defined as the highest frequency sinusoid that can be resolved at a given sampling rate. If  $\Delta t$  is the sampling period,

$$f_{Nyq} = \frac{1}{2}f_s = \frac{1}{2\Delta t}$$
 (5-13)

Aliasing is the association of a high frequency component to an incorrect, lower frequency and occurs when a signal contains components having frequencies above  $f_{Nyq}$ . These higher harmonics are folded back about  $f_{Nyq}$  into the frequency domain below,



Figure 5-4 - Spurious 5 Hz sine wave from sampling a 100 Hz signal at  $f_s = 95$  Hz

adding to the valid components already there. For example, Figure 5-4 shows what happens in the time domain when a 100 Hz sinusoid is sampled at a frequency of 95 Hz. The result is a spurious 5 Hz signal.

One can usually tell if aliasing has occurred by inspecting the frequency spectrum generated by the DFT. If the magnitudes of the harmonics are not at, or close to, zero in the neighbourhood of the Nyquist Frequency, then aliasing is probable, and a higher sampling rate must be employed to accurately represent the sampled signal.

When using an arbitrary waveform to generate a strain having components in a certain range of frequencies, care must be taken when setting the sampling rate if there are significant harmonics outside the desired bandwidth. The sampling frequency must

64

be set high enough to resolve accurately the undesired harmonics as well or they will be aliased back into the desired range. For example, the DFT of the PRBS function (see section 5.4) has a  $|\sin(x)/x|$  shape. Usually only the first few peaks in the transform are of interest, but the higher frequency harmonics must also be resolved when sampling or they will reflect back from  $f_{Nyq}$  and distort the information in the desired range.

## 5.3.2 Time and Frequency Domain Scaling

Scaling in the time and frequency domains are closely related. Fixing the sampling period,  $\Delta t$  (or its inverse,  $f_s = 1/\Delta t$ ), and the number of samples collected, N, sets the ranges of both the time and frequency axes. The time axis runs from 0 to T, where  $T = (N-1)\Delta t$ , in increments of  $\Delta t$ . The frequency axis runs from 0 to  $f_{Nyq}$ , where  $f_{Nyq} = \frac{1}{2}f_s$ , in increments of  $\Delta f$ , where  $\Delta f = f_s/N$ . If N is held constant, increasing the resolution in one domain causes a decrease in the other; as  $\Delta t$  is decreased to get better time domain resolution,  $\Delta f$  will increase. Two units of frequency are in common use: cycles per second, f (Hertz), and radial frequency  $\omega$  (radians/second) with  $\omega = 2\pi f$ .

For any real-valued time signal, the magnitude of the transform in the negative frequency domain is a mirror image of that in the positive domain (an even function), while the phase is duplicated but inverted (an odd function). We are always dealing with real time signals, so only the range 0 to  $f_{Nyq}$  is of interest; the other half of the transform contains a duplication of information. Some DFT routines assume a real input signal and only return the first N/2+1 points, corresponding to the range 0 to  $f_{Nyq}$ , thus eliminating the duplication.

This duplication of information is why the amplitude of a frequency harmonic is only half the value of the amplitude in the time domain. Half of the amplitude appears in the positive frequency domain, and half appears in the negative domain.

#### 5.3.3 Leakage

When setting the data acquisition parameters for an experiment (sampling rate and number of points), care must be taken to ensure that an integral number of cycles will be sampled. The length of the cycle is then harmonically related to the length of the

<u>,</u> ),

sampling window, and the frequency components of the signal fall exactly on the discrete points in the DFT. When a non-integral number of cycles are sampled, the actual frequency of a component falls between two of the discrete frequency points, and the amplitude is split between them. As a result, the amplitude is reduced and spread over more than one frequency node. This phenomenon is called leakage. Leakage also has a considerable effect on the phase of the frequency signal.

A spurious discontinuity is introduced into a waveform when a non-integral number of cycles are sampled, as a result of the assumption of the periodicity of the signal. The last points in Figure 5-5a and Figure 5-5b (open symbols) are the first points



Figure 5-5 - The effects of leakage due to assumed periodicity



Figure 5-5 - The effects of leakage due to assumed periodicity

# 5.3.4 Alternating versus Simultaneous Data Acquisition

The frequency analysis techniques assume that stress and strain signals are sampled at the same time. If they are not, an additional erroneous phase shift between the stress and strain is introduced, which affects the calculated value of  $\delta$ .

The RDA does not have simultaneous sample and hold for all channels but performs sampling in an alternating fashion. The analog to digital converter runs at twice the desired sampling frequency and scans the stress and strain channels in succession, retrieving data at the desired rate but not simultaneously. The phase shift due to this method of sampling was calculated as shown below, and a correction was applied to the data.



Figure 5-6 - Relative phase shift due to alternating sampling

frequency. Since the DFT calculation assumes simultaneous sampling, the "o" wave is effectively shifted to the left by one alternating sample period to the position of the dotted line "\*" wave (to line up with the "x" wave). An alternating period is the equivalent of one half of a simultaneous period, so that the additional phase shift  $\delta_a$  in radians is

$$\delta_{a} = 2\pi \frac{\frac{1}{2}\Delta t}{T_{0}} = \pi \Delta t f_{0} = \pi \frac{f_{0}}{f_{s}}$$
(5-14)

where  $\Delta t = 1/f_s$  is the simultaneous sampling period,  $T_0 = 1/f_0$  is the period of the sine wave, and  $\sin(2\pi f_0 t - \delta + \delta_a)$  is the equation of the "\*" wave. The phase shift,  $\delta_a$ , depends on the sampling rate,  $f_s$ , and the frequency of the waveform being sampled,  $f_0$ .

The simplest way to apply the correction given by (5-14) is to transform whichever waveform is being sampled second (the "o" wave in Figure 5-6) to the frequency domain in polar form and then subtract the correction from the phase of the waveform at each frequency. While  $f_s$  is held constant at the value used during data acquisition, the  $f_0$  value used is the frequency of the point being corrected;  $\delta_a$  is a linear function of frequency, so that its value is increasing as it is subtracted from the higher frequency phase components. The waveform can then be converted back to Cartesian coordinates or restored to the time domain. Only one of the signals should be treated, since it is the relative phase between the signals that is being corrected. Note also that the signal frequency and the sampling frequency must be in the same units, either Hz or radian/s; mixing units requires a factor of  $2\pi$  in the numerator or denominator of the equation.

## 5.4 Waveforms of Special Interest

While any periodic waveform can be in theory used to generate a strain history for dynamic measurements, some waveforms are more useful than others. Good waveforms have either a flat frequency spectrum with a high amplitude over as wide a range as possible or a number of sharp peaks at specific frequencies of interest. A composite waveform created from two or more sine waves added together will produce results at the discrete frequencies of the sine waves, while an exponential strain function has a broad frequency spectrum, particularly at lower frequencies [34,35,36]. See Nelson and Dealy [37] for a more complete list of suggested waveforms and their advantages.

In order to track the cross-over point of G' and G" curves for a series of polypropylenes having different molecular weights, a broad spectrum capable of reaching high frequencies (up to 100 rad/s) was needed. A pseudo-random binary sequence waveform was selected for use with this system and is described below.

## 5.4.1 PRBS Waveforms

A pseudo-random binary sequence (PRBS, sometimes called a binary maximum length sequence, or BMLS) is a waveform commonly used in stochastic system identification to obtain an estimate of a system's impulse response. It has almost the same auto-correlation as white noise (a single impulse at lag 0) but is cyclic, so that only one period of the waveform need be sampled to obtain all necessary information. It also

69

has a fairly flat frequency spectrum, the range of which can be controlled through the parameters,  $n_B$  and  $\Delta t_B$ .

The PRBS is a series of steps between two signal levels. It is periodic with a period  $T_B$ , and can change levels only at certain discrete times,  $k\Delta t_B$ , where k is an integer and  $\Delta t_B$  is the minimum discrete time interval for a step. The PRBS consists of a chain of "up" and "down" states of different lengths, with the number of "up" states equal to one more than the number of "down" states. The total number of discrete time intervals, N<sub>B</sub>, is a function of the "degree"  $n_B$  of the PRBS, where

$$N_B = 2^{n_B} - 1$$

$$T_P = N_P \cdot \Delta t_P$$
(5-15)





The frequency spectrum of a PRBS has a  $|\sin(x)/x|$  envelope, as shown in Figure 5-8. The 3 db dropoff occurs at approximately  $f_{max} = 1/(3\Delta t_B)$  Hz, giving the



PRBS a useful range conservatively estimated as  $f_{min}=1/(N_B \cdot \Delta t_B)$  to  $f_{max}$  (in many cases, the PRBS gives useful results far beyond the suggested  $f_{max}$  limit, as in the sample experiment in section 5.5). The amplitude reaches zero for the first time at  $f=1/\Delta t_B$ .

The drive systems that provide the strain for dynamic mechanical measurements cannot provide the infinite shear rate necessary to generate the steps required for an ideal PRBS. Most systems can, however, provide a steep ramp. In fact, such high-speed ramps are used to determine the relaxation spectrum in the time domain. Thus, the PRBS can be thought of as a series of stress relaxation experiments, repeated at varying intervals to obtain the desired frequency spectrum; in fact Vratsanos et al. [39] used step strains and Fourier transforms to generate viscoelastic data. The response of the drive motor will likely cause some irregularities in the frequency spectrum. However, as long as the **actual** strain (as opposed to the commanded strain) is used in the analysis of the data, there is little effect on the final result. If high frequency harmonics are not desired and are causing aliasing problems, filtering the strain waveform can reduce their amplitudes. The filtering may be performed either digitally by programming the waveform generator or directly on the analog control signal as it is sent to the rheometer drive controller.

A signal that resembles the PRBS is a randomly switched bi-level waveform. At each time point  $k \cdot \Delta t_s$  (where k is an integer), the signal has a certain probability of



Figure 5-9 - Randomly switched waveform,  $p_s = 50\%$ ,  $N_s = 31$ ,  $\gamma_s = 15\%$ 

switching to the opposite state. This is shown in Figure 5-9, where the probability of switching at a given point is 50%. This waveform is simpler to generate than a PRBS but doesn't have the same well-defined statistical properties, particularly if a small number of steps is used. In Figure 5-9, the mean "up" time is 38.7%, considerably lower than the ideal value of 50%.

## 5.5 A Sample DMA Experiment

We now describe in detail the design and analysis of an actual experiment using a PRBS strain signal. The polymer sample was a silicone putty (poly dimethylsiloxane) having room temperature properties similar to those of the polypropylene used in the visbreaking process. A rotational rheometer (Rheometrics RDA II with the arbitrary waveform option and an external waveform generator) with 25 mm- diameter parallel disk fixtures was used. The gap was 1.5 mm, and the temperature was 30°C.

First we select the frequency range over which results are desired and determine the PRBS parameters,  $n_B$  and  $\Delta t_B$  that will provide harmonics in this range. In general, a value of  $\Delta t_B$  is chosen first to fix the upper end of the frequency range. The width of the range is then governed by the length of the PRBS, i.e., by  $n_B$ , which determines how many steps will be taken. In this case, a bandwidth of .06 to .6 Hz, corresponding roughly to .4 to 4 radians/s, was chosen. The PRBS will expand the high frequency end of this range if we use the conservative frequency max/min estimates of section 5.4.1 to calculate the parameters. Once the frequency range has been selected, theoretical values for the minimum discrete time step  $\Delta t_B$  and degree  $n_B$  were determined using equation (5-15). Convenient values were then chosen to closely match theoretical values as closely as possible:

$$f_{\text{max}} = \frac{1}{3\Delta t_B} = .6Hz$$
$$\Delta t_B = .55555s = \underline{\Delta t_B} = .5s$$
$$f_{\text{min}} = \frac{1}{N_B \Delta t_B} = .06Hz$$
$$N_B = 33.3 \Rightarrow \underline{n_B} = 5, \ \underline{N_B} = 31steps$$

In this case,  $\Delta t_B$  was set at 0.5 seconds, close to the theoretical value of 0.5556 seconds. The theoretical value of N<sub>B</sub>, which is 33.3, leads to selecting n<sub>B</sub>=5, giving N<sub>B</sub>=31 steps. The frequency bandwidth calculated for the test parameters is  $f_{min} \approx .065$  Hz and  $f_{max} \approx .667$  Hz, close to the desired range. The size of the step strain,  $\gamma_B$ , was chosen to be 30%, which is in the linear viscoelastic region for this polymer and gives a reasonable stress pulse amplitude.

Once the strain signal was fixed, the data sampling rate had to be established. There were several criteria that f, had to satisfy:

- The frequency selected should be high enough to resolve all of the significant high frequency harmonics in the PRBS to avoid aliasing.
- To avoid leakage, each step in the PRBS should be sampled an integer number of times.

To sample the harmonics at  $\hat{t}_{max}$ ,  $\hat{t}_{Nyq}$  must be at least 0.667 Hz. Figure 5-8 shows the transform of a sample PRBS with  $n_B=5$  and  $\Delta t_B=.5$  s; it is obvious that a much higher sampling rate than  $f_s=2f_{max}=1.333$  Hz will be required. For this particular test,  $f_s=80$  Hz was chosen, giving  $f_{Nyq}=40$  Hz. While the harmonics in Figure 5-8 are not quite zero at 40 Hz, they are small enough that they will have little effect. The region affected by any aliasing will be in the range of 20-40 Hz, well above the range of interest. In addition, high frequency harmonics were damped by the motor drive in the actual strain signal, further reducing any aliasing. The RDA control computer is capable of storing up to 1600 points per experiment; with  $\Delta t_B=.5$  s, 40 points per step will be sampled giving 1240 points for the entire waveform.

When applying the PRBS strain to the sample, care was taken to ensure that all start-up transients had died out before starting to acquire data. The results of a time-



Figure 5-10 - Stress relaxation experiment; silicone putty at 30°C

domain stress relaxation experiment gave an estimate of the time required for the fluid to adapt to a sudden change in strain. The stress relaxation curve for the silicone putty at 30°C is displayed in Figure 5-10. The stress drops off rapidly and is almost zero after 6 seconds. Allowing a few additional seconds as a margin for error, data acquisition was initiated 15 seconds after starting the strain waveform. Timing the start of acquisition to coincide with the start of the PRBS was not necessary. As long as an integer number of PRBS cycles is sampled, the beginning and end of the sampled waveform will be continuous.

Once data for the experiment were collected, they were converted to proper units (stress in Pa and strain in strain units). Figure 5-11 shows the time domain results. There was a slight strain distortion in each shear step; the initial part of a step was sharp, but the top was slightly rounded by the motor response. This slightly lowered the high



Figure 5-11 - PRBS test: stress and strain results (time domain)

frequency content of the signal. The stress response looks like a series of stress relaxations similar to Figure 5-10.

A DFT subroutine was then used to transform  $\sigma(t)$  and  $\gamma(t)$  into the frequency domain. Since the number of samples was not an even power of two, a normal FFT algorithm could not be used. MATLAB V3.5's FFT function, which accepts any number

e,

of data points and is almost as fast as a regular FFT subroutine, was used to transform the data.

Alternating data sampling was used, with  $\sigma(t)$  sampled first and  $\gamma(t)$  second. The correction mentioned in section 5.4.2 was applied to the strain. After transforming  $\gamma^*(f)$  to polar coordinates ( $|\gamma^*|$  and phase in radians), we subtracted  $\delta_a = \pi f/f_s$  from each phase value, where f was the frequency of the component being corrected and f, was the



Figure 5-12 - Stress and strain: frequency domain results

sampling frequency, 80 Hz. This is an important correction, as  $\delta_a$  becomes significant at high frequencies.

Examination of the magnitudes of  $\sigma^*(f)$  and  $\gamma^*(f)$  in Figure 5-12 show that the higher frequency harmonics fell to 1/200th of their low frequency amplitudes before reaching  $f_{Nyq}=40$  Hz. This suggests that the results are free of any aliasing effects. Notice that any fluctuation in the amplitude of  $\gamma^*(f)$  is matched in  $\sigma^*(f)$  so that the ratio between them, G<sup>\*</sup>(f), is a smooth function.

Point by point complex division of the  $\sigma^*(f)$  function by  $\gamma^*(f)$  gave the function  $G^*(f)$ , which is shown in Figure 5-13. The magnitude and phase of  $G^*$  were valid beyond the original estimate of  $f_{max}$ . The PRBS data compare well with data obtained using



Figure 5-13 - PRBS experiment results compared with single point data from the same sample.

single frequency tests with the same sample, with acceptable data obtained over two decades. At the high frequency limit, the signals are very noisy; here the strain amplitudes became so small that the stress and strain measurements were lost in the system noise. The time necessary to perform the experiment is much less than that required to generate single point measurements over the same frequency range. The entire measurement is performed in slightly longer than the period of the lowest measured frequency.

## 5.6 Complex DMA using the In-line Rheometer

Although it was shown that DFT analysis of complex waveforms is a viable method of obtaining DMA data using the RDA II, it remained to apply the same method to the in-line rheometer (ILR). Experiments were performed using the torsion spring SST, with no polymer flow from the extruder. The ILR was flushed with Profax 6631 polypropylene (no peroxide added) before measurements were taken to ensure that there was fresh polymer in the gap. The lack of flow during the measurements eliminated any effects due to pressure flow in the shearing gap, as well as any direct pressure effects on

the SST. The temperatures of the rheometer and polymer were allowed to come to steady state, so the polymer in the shearing gap could be assumed to be at 200°C, which was the setpoint temperature of all of the rheometer heater zones.



Figure 5-14 In-line rheometer PRBS experiment result, Profax 6631,  $\Delta t_B = 0.0667$  s,  $n_B = 5$ ,  $f_s = 250$  s, 517 data points.

The G'-G" crossover occurs somewhere between 10 and 100 rad/s (1.6 and 16 Hz), depending on the peroxide concentration. Many PRBS waveforms were evaluated to find one that gave the desired frequency content and that the drive motor was capable of generating. Figure 5-14 shows a PRBS with  $\Delta t_B = .067$  s and  $n_B = 5$  (or  $N_B = 31$  steps). The entire test took slightly longer than two seconds to perform, which is similar to the duration of a viscosity test. The time domain responses of the ILR are seen to be noisier than the stress and strain signals of the RDA, even with the low-pass linear filters in the

circuit (see section 2.4.1). Most of this noise is thought to be caused by the motor controller for the ILR drive.

One problem with the stress signal was its magnitude. The SST signal was about  $\pm 0.5$  V, or 1 V<sub>PP</sub> on a full scale of 10 V, for the highest weight average molecular weight material that the rheometer would be required to measure. At high peroxide concentration levels (400 ppm), the stress signal would be reduced by approximately 50%, leading to a substantial signal to noise reduction. At lower values of M<sub>w</sub>, larger strain amplitudes have to be used. Care has to be taken, however, not to exceed the linear viscoelastic limits of the polymer.

The strain signal in Figure 5-14 has been slightly distorted by the motor response, with the sharp edges of the steps slightly rounded off. This slightly reduced the frequency content of the waveform, but otherwise the signal is very good. In some experiments, the baseline of the waveform drifted during the test because the motor controller operated in a controlled speed rather than controlled position mode. The null motion signal occasionally had to be re-zeroed to avoid these drifts.



Figure 5-15 DFT of stress and strain data from Figure 5-14.

The frequency domain representation of the data in Figure 5-14 is displayed in Figure 5-15. These results are comparable to those shown in Figure 5-12 for the experiment performed with the RDA, with the sin(x)/x envelope characteristic of the PRBS. The data were sampled at  $f_s = 250$  Hz, giving  $f_{Nyq} = 125$  Hz. This was more than six times higher than the region of interest (up to about 20 Hz), giving protection against

aliasing. The linear phase filters also remove high frequency components; at 125 Hz, the filters reduce harmonics to .8% of their original amplitude.



Figure 5-16 G', G" curves calculated from data in Figure 5-14. The points are single point measurements performed on the RDA.

The stress and strain data were sampled by the "alternating sampling" method. The correction mentioned in section 5.3.4 was applied to the phase of the strain signal, and the storage and loss modulus curves were then calculated. Single frequency values of G' and G" for the same material, measured using the RDA (25 mm plates, 200°C), are displayed in Figure 5-16 along with the ILR results. The results contain considerable noise, and the crossover point is difficult to identify, but it appears to be between 1.5 and 2.5 Hz. The single point measurements indicate a crossover frequency of 2.5 Hz. The loss modulus in particular is quite low compared to the RDA data.

Changing the format of the results, the complex modulus is displayed in polar coordinates in Figure 5-17.  $|G^*(f)|$  is noisy, but it has approximately the correct magnitude until about 8 Hz, when it starts to drop off slightly. The PRBS response goes to zero at 15 Hz, which is what causes the erratic values in that region. The phase of  $G^*(f)$ ,  $\delta(f)$ , deviates considerably from the single point measurements. The signal is very noisy and consistently below the RDA values.  $\delta$  is very important in this application, because it determines the location of the G'-G" crossover;  $\delta$  must be  $\pi/4$  at the crossover point of the curves.



Figure 5-17 The magnitude and phase of the  $G^*(f)$  function calculated from the ILR data. Single points are RDA data.

Experiments were performed with the ILR using sine waves to get single point results over a range of frequencies. The results were the same as for the PRBS tests; while the magnitude of  $G^*$  was approximately correct, the phase angle  $\delta$  was always below the RDA results.

#### 5.6.1 SST Frequency Response Characteristics

Considerable phase distortion was introduced into the DMA measurements performed using the ILR. Three possible sources for this distortion were the strain measurement, the stress measurement and the linear phase filters used for anti-aliasing. Torques on the rotating shaft of the rheometer were calculated to estimate the amount of twist in the shaft under load and were found to be negligible, as mentioned in section 2.4.1. The phase response of the strain measurement device was not determined experimentally, but product literature stated that it was negligible below 40 Hz; the range of interest for these experiments was considerably lower than this limit. The responses of the matched, linear phase filters were verified, and they were found to be identical to within 0.005 radians.

Step tests were performed on the SST to estimate its dynamic response characteristics. The step in stress was simulated using the calibration apparatus. A weight was suspended from the calibration wire, and the stress was allowed to come to



Figure 5-18 Response of the SST to a step in stress with and without polymer present in the rheometer cavity.

steady state. Then the weight was suddenly removed, and the response of the SST recorded at 2500 Hz. The linear phase filters were removed for these tests to allow a wide frequency spectrum to be inspected. A 50 g weight was used to generate the responses shown in Figure 5-18, simulating a stress step of approximately 8000 Pa; the same order of magnitude as the PRBS experiment stress readings. The response of the SST when there was no polymer in the SST cavity is clearly much faster than when the cavity was full. The difference between the no polymer response and the ideal response is due to lags in the electronics, inertia in the SST and non-idealities in the stress step simulation (the "step" was actually a fast ramp). When polymer was present, the drag of the polymer on the SST beam and the squeezing flow in the gap around the active face damped the response to the stress step. Before each response test, steps were taken to minimize the effect on the response of polymer acting on the surface of the active face. The shearing drum was rotated at high shear rate, with no flow of polymer from the extruder. This removes most of the polymer from the shearing gap, and after several seconds, the SST indicates close to zero stress, even with the drum rotating.

A frequency analysis of the step responses was then performed. In Figure 5-19, the magnitudes of the harmonics in the frequency range of interest are displayed. The ideal step has a  $\sin(x)/x$  envelope similar to the PRBS, which reaches zero for the first time at 13.6 Hz. Both SST responses fall off well before 10 Hz, at approximately 4 Hz



Figure 5-19 Frequency analysis of stress step data in Figure 5-18; magnitude of the frequency components.

with polymer present, and 6 Hz when it is not. Both responses are greater than the ideal step at low frequencies because of imperfections in the stress step (the small dip before the main response). The presence of polymer in the SST clearly diminishes the response at higher frequencies, leading to low  $|G^*|$  values at frequencies above 8 Hz.

The phase of the SST response was also examined. The phase difference between the ideal response and the SST responses is plotted in Figure 5-20. The no-polymer



Figure 5-20 Phase difference between ideal step and SST response.

response has a small lag at low frequencies, due to imperfections in the stress step. At higher frequencies, the phase drops off further, due to the mechanical response of the

SST and the probe electronics. With polymer in the SST cavity, the phase lag is much more severe. While difficult to predict exactly because of the spike in the waveform at 10 Hz, the with-polymer phase lag is the same order of magnitude as the phase of  $G^*$  and becomes greater at high frequency.

## 5.6.2 Conclusions

The drag force exerted by the polymer on the SST beam is a complex function of the viscosity of the polymer and the speed of the motion [40]. While the distances actually moved by the transducer beam were very small (less than 0.002 mm), the speed of the motion was important; the drag force varied with the type of motion performed as well as with the polymer properties. No method was found that would give results of sufficient accuracy for G'-G" crossover determinations. The problem lies in the SST; the internal cavity must be sealed from the polymer to prevent it from damping the response.

The difficulties with the SST response were encountered under ideal conditions. With the visbreaking process operating, pressure flow effects in the shearing gap, pressure effects on the SST and temperature effects would further compound the error in the DMA measurements. The problems would be more severe at higher frequencies, where the crossover point for the visbreaking process is found. It was decided, therefore, that DMA measurements would not be used for process control in this research. Steady shear viscosity, which does not depend on SST dynamics, was used instead.

84

# CHAPTER 6 SHEAR VISCOSITY MEASUREMENT TECHNIQUES

## 6.1 Introduction

Side stream (or on-line) rheometers have an advantage over in-line rheometers in at least one respect. Because the polymer is long in transit, there is sufficient time to condition the melt before a measurement is taken. An in-line rheometer (ILR), on the other hand, must make a measurement at whatever pressure, temperature, and flow rate the process imposes. Compensation for pressure flow in the rheometer and temperature effects must be performed to produce viscosity values referred to standard conditions.

The ILR developed for this project had a pressure gradient along the shearing gap, causing a pressure flow to be superposed on the drag flow generated by the rotating drum. Compensation for this is not trivial because polymer melts are non-Newtonian. Temperature compensation was also required, since the rheometer had only a limited ability to control sample temperature.

The speed of the response of the rheometer was governed by how quickly fresh material could be drawn from the process stream into the shearing gap. Several methods of doing this were examined, and the fastest one was incorporated into a viscosity measurement procedure. The accuracy and repeatability of viscosity measurements were then examined to ensure that the rheometer could function adequately as a process control sensor.

#### 6.2 Pressure Compensation

## 6.2.1 Effects of Pressure on the Wall Stress Calculation

There are three ways in which pressure in the rheometer affects viscosity measurement. One is the pressure acting directly on the shear stress transducer (SST); the second is pressure driven flow that causes false stress readings; and the third is a

coupling of the first two. All three must be accounted for if accurate viscosity measurements are to be made.

Broadhead [12] used a dead-weight tester to determine the effect of static pressure on the SST output signal. It was hypothesized that imperfections in the SST (slight nonparallelism, non-zero tolerances, etc.) caused small deflections of the beam (angular and axial) when the SST was placed under pressure (see section 2.2.1). This led to spurious shear stress indications as the pressure fluctuated in the rheometer. Broadhead modelled this relationship and found it to be linear. He used the following correction:

$$V_{SST}(corrected) = V_{SST} + a_1 P$$
 (6-1)

where **P** is the absolute pressure at the SST,  $V_{SST}$  is the signal from the SST, and  $a_1$  is the correction factor. Broadhead found  $a_1 = 0.111 \pm 0.007$  V/MPa for his experiments.

In this study, the effect on the SST baseline signal of both the absolute pressure  $\overline{P}$  and the pressure drop  $\Delta P$  were studied simultaneously, *in situ*, with the extruder running but the rotating drum of the rheometer stationary.  $\Delta P$  is defined as  $P_1 - P_2$ , the upstream pressure minus the downstream pressure, and is therefore positive.  $\overline{P}$  is the average of  $P_1$  and  $P_2$ , a good estimate of the pressure at the SST located midway between the pressure sensors.

The pressure drop causes a flow through the shearing gap. For fully-developed pressure flow in a slit,

$$\sigma_W = \frac{\Delta P}{L} \cdot \frac{h}{2} \tag{6-2}$$

regardless of the properties of the fluid in the gap. For  $L_p = .08$  m (the distance between the pressure sensors), gap height h=.001 m,  $\sigma_w$  in Pa and  $\Delta P$  in MPa, the wall stress due to pressure flow is calculated from eqn (6-2) as:

$$\sigma_w = 6.25 \times 10^3 \Delta P \tag{6-3}$$

Pressure and pressure drop are dependent on each other for a given rheometer geometry. Experiments to determine the effects of pressure were performed at varying flow rates, using several die geometries to vary the  $\overline{P}$  versus  $\Delta P$  relationship ( $\overline{P}$  and  $\Delta P$  are interdependent for a fixed geometry). Three die configurations were used; a small diameter die, a larger diameter die and no die at all. The flow rate was varied randomly between 4 and 12 kg/h; SST output and pressures were measured at each feed rate for each die. The pressure effects should be independent of the properties of the resin used; the tests were run with two polypropylene resins, Profax 6631 (MFR=2 g/10 min) and Profax PD701 (MFR=30 g/10 min), to confirm this.

Broadhead's analysis of the static pressure effect and the theoretical predictions for the pressure flow effect indicate that both should be linear. The following model was fitted to the data using the MATLAB routine FMINS.

$$V_{\rm SST} = a_1 \overline{P} + a_2 \Delta P + a_3 \tag{6-4}$$

Figure 6-1 - Regression results: the effect of P and  $\Delta P$  on the SST signal. The effect of  $\Delta P$  is subtracted from  $V_{SST}$  when graphing the P effect in (a), and vice versa when graphing (b).

The parameters  $a_1$  and  $a_2$  are in units of volts per unit pressure, while  $A_1$  and  $A_2$  are the same parameters converted into units of stress per unit pressure, for use in the stress cal-
culation equation. The constant  $a_3$  accounts for the offset in the voltage measurements. The observed values of  $a_1$  were 0.111 V/MPa for Profax 6631 and 0.075 V/MPa for Profax PD701; the value computed using data for both resins and used in subsequent viscosity calculations was  $a_1=0.107$  V/MPa (shown in Figure 6-1a). These values, particularly the one for Profax 6631 alone, match the results of Broadhead very well. The effect of the pressure flow was also in the expected range;  $a_2=.388$  V/MPa for resin B8,  $a_2=.365$  V/MPa for resin B2, and as shown in Figure 6-1b,  $a_2=0.379$  V/MPa when all data are used in the regression. Using a calibration constant of 16 kPa/V, the shear stress due to the pressure flow was  $A_2=6.1x10^3$  Pa (stress)/MPa (pressure drop), which corresponds very well to the theoretical value shown in eqn (6-3). Pressure losses due to entrance and exit effects cause the actual value to be lower than theoretically predicted.

These two corrections were used to adjust the stress measurement before the calculation of viscosity. If the absolute pressure correction is converted to appropriate units,  $A_1=1712$  Pa (stress)/MPa (pressure) for an SST calibration of 16 kPa/V, the stress calculation equation is

$$\sigma_W = \sigma_M - \sigma_B + A_1 (\vec{P}_M - \vec{P}_B) - A_2 \Delta P_B$$
(6-5)

where B and M subscripts refer to measurements taken during baseline sampling and during shearing respectively. The first correction term accounts for any difference in the absolute pressure between the baseline and shearing measurements, while the second term corrects for the non-zero baseline value due to pressure flow.

The data in Figure 6-1 show considerable scatter; many points were required to obtain a statistically meaningful fit. Aside from electronic noise and vibration, there is a third pressure effect causing noise that has to do with the compressibility of the polymer. Whenever there is a change in  $\overline{P}$ , the density of the polymer changes. This leads to flows into and out of the cavity of the SST through the annular gap around the active face (see section 2.2), causing flow across the face and a spurious stress measurement. This effect is demonstrated in Figure 6-2. When flow was started, the pressure in the rheometer went from atmospheric to operating pressure in 7 s. A large start-up



Figure 6-2 Start up transient of SST signal, resin B8 flow stepping from 0 to 6 kg/h, small die on the extruder.

transient in the SST output of approximately 2 V in magnitude occurred as the pressures equalized between the interior of the rheometer and the cavity in the SST, requiring an additional 15 s to settle out.

The flow of polymer in the SST was simulated numerically to investigate the third pressure effect. Density and pressure in the SST cavity ( $P_c$  and  $\rho_c$ ) were modelled as functions of time to see how they are affected by the pressure in the main rheometer cavity. The relationship between the pressure and density of the polymer is modelled by the compressibility equation:

$$\rho_{C} = \rho_{0}(1 + \beta(P_{C} - P_{0}))$$
 (6-6)

where the compressibility of polypropylene,  $\beta$ , was taken to be 0.001 with pressure in MPa [41], and the melt density  $\rho_0=740$  kg/m<sup>3</sup> at a reference pressure of P<sub>0</sub>=0.1 MPa. From a mass balance on the polymer in the SST cavity,

$$\frac{d\rho_C}{dt} = \frac{Q_A \rho_A}{V_C}$$
(6-7)



Figure 6-3 Sample pressure simulation result modelling the response to a pressure step in the rheometer from 0 to 1.75 MPa

where  $V_c$  is the volume of the cavity. The density in the annular gap around the active face of the SST,  $\rho_A$ , was taken to be the average of the density in the cavity and that in the rheometer channel.  $Q_A$  is the volumetric flow of the melt through the annular flow channel, where fully developed flow of a power law fluid is assumed. From Tadmor and Gogos [42],

$$Q_{A} = \left(\frac{n\pi R^{3}}{1+2n}\right) \left(\frac{R\Delta P}{2mL}\right)^{\frac{1}{n}} (1-K)^{\frac{1}{n}+2} F(n,K)$$
(6-8)

S.

**R**=8.3 mm is the outside radius of the annulus, while **KR** is the inside radius. **L** is the length of the flow channel, taken to be 1 mm, and **n** and **m** are the power-law parameters. F(n,K) is a non-linear flow factor that is approximately one for n=0.4 and K=0.9844. Note that the fully developed flow assumption is not completely valid in this situation, since the flow channel is too short (the length to height ratio for the annulus is approximately 8). Entrance and exit effects will reduce flow through the gap, and the model will thus underestimate the length of time required to achieve a steady state pressure.

In Figure 6-3, we see that a significant time is needed for the SST cavity pressure to become equal to the pressure in the rheometer when a 1.75 Mpa pressure step is introduced in the rheometer. The model suggests there is about 5 seconds of rapid change (high flow rates into the cavity) and then a long transient, which agrees qualitatively with the start-up transient in Figure 6-2. Large pressure fluctuations would have a similar response. Some thought was given to compensating for the compressibility effect, but useful models would be dynamic in nature and heavily dependent on the physical characteristics of the polymer (rheological properties and compressibility). Any scheme giving a reasonable correction would be very complex to implement and not worth the effort in terms of the reduction in noise.

When the rheometer is at operating pressure, pressure fluctuations from the extruder are generally small enough that the compressibility effect can be ignored. However, there is a region of viscosity, from approximately 700 to 750 Pas, where



Figure 6-4 Sample of the effect of surging on a stress measurement, with  $\gamma = 25$  1/s.

surging occurred in the extruder. The magnitude of the pressure change depends only very slightly on screw speed and feed rate but strongly on viscosity. Figure 6-4 shows variations in  $\overline{P}$  of 0.75 MPa in magnitude, which cause considerable noise in the stress

signal. To minimize the effects of these fluctuations, the baseline and shearing measurements were averaged over 2 to 3 s. Times longer than this were not practical because of restrictions on the rheometer cycle time (see section 6.5). Even with these precautions, the standard deviation of viscosity measurements in the 700 to 750 Pass range was higher than for other viscosity regions.

#### 6.2.2 Pressure and Non-Newtonian Effects in Viscosity Calculation

During a viscosity measurement the shear stress transducer detects the wall shear stress  $\sigma_w$  in the gap. This stress measurement has two components, one due to the drag flow caused by the rotating drum, and one due to the pressure flow through the gap. Compensation for the pressure flow must be implemented to obtain an accurate viscosity value. The curvature of the rotating drum is neglected to develop a model of the flow

$$y=h \qquad V \Longrightarrow$$

$$y=h/2 \qquad y=0 \qquad x \qquad y*$$

$$y=0 \qquad \Delta P \ FLOW$$

Figure 6-5 Slit flow, with the pressure flow in the same direction as the drag flow. in the gap, with the stationary wall (where the wall stress is measured) at y=0, and the moving wall (the rotating drum surface) at y=h, as shown in Figure 6-5. This simplification is valid because the annular shearing gap, h=1 mm, is only 4% of the radius of the shearing drum.

The stress profile is given by Cauchy's equation:

$$\frac{\partial \sigma_{yx}}{\partial y} - \frac{\partial P}{\partial x} = 0$$
 (6-9)

where  $\sigma_{yx}$  is the shear stress,  $\sigma$ , and  $\partial P/\partial x = -\Delta P/L = (P_U - P_D)/L$ . Integrating with the boundary condition  $\sigma = \sigma_W$  at y = 0 gives:

$$(6-10) \quad \sigma = \sigma_W - \frac{\Delta P}{L} y$$

which is true for all fluids, regardless of  $\sigma(\gamma)$  behaviour. With the wall stress measurement from the SST, and knowing  $\Delta P/L$  from the pressure transducers in the rheometer, the stress profile in the gap can be calculated for any material.



Figure 6-6 Shear rate profiles of a Newtonian fluid in the gap between two parallel plates, with (solid line) and without (dashed line) a pressure drop.  $\dot{\gamma}_{rag}=30$  1/s,  $\Delta P=.62$  MPa.

When there is no pressure drop along a channel of height h and all polymer deformation is due to the drag flow caused by the wall at y=0 moving at speed V, the shear rate in the gap is uniform and equal to V/h, as shown by the dashed line (30 s<sup>-1</sup>) in Figure 6-6. If a pressure drop  $\Delta P/L$  is added, the shear rate is no longer constant. To calculate the shear rate profile for a Newtonian fluid, we simply add the shear due to the pressure flow (second term on RHS in Eqn (6-11)) to that caused by the moving wall:

$$\dot{\gamma}_{N}(y) = \frac{V}{h} - \frac{\Delta P}{L\eta_{N}}(y - \frac{h}{2})$$
 (6-11)

where  $\eta_N$  is the Newtonian viscosity. Substituting  $\eta_N \equiv \sigma/\dot{\gamma}$  and using Eqn (6-10), the Newtonian shear rate profile becomes

$$\dot{\gamma}_{N}(y) = \frac{V}{h} \left( \frac{\sigma_{W} L - \Delta P y}{\sigma_{W} L - \Delta P \frac{h}{2}} \right)$$
(6-12)

which is the equation of the solid line in Figure 6-6. The only place where there is no deformation due to  $\Delta P$  is along the centre line, y=h/2; this is the only place where the polymer is being sheared at  $\dot{\gamma}$ , the desired shear rate. Using (6-10) to calculate the stress at y=h/2, the Newtonian viscosity is

$$\eta_N = \frac{\sigma_W - \frac{\Delta P}{L} \cdot \frac{h}{2}}{\frac{V}{h}}$$
(6-13)

where V is fixed and  $\Delta P$  and  $\sigma_w$  are measured.

Complications arise for non-Newtonian fluids. The pressure and drag flow strains are no longer additive, and it is difficult to determine the shear rate profile in the gap without assuming a  $\sigma(\gamma)$  function. The method outlined here was developed by Broadhead [12], and was inspired by an earlier method developed by Schümmer [43] to determine the true viscosity from measurements in a capillary rheometer without using the Rabinowitch correction.

For given  $\sigma_w$ ,  $\Delta P$  and V, the shear rate profiles for Newtonian and shear thinning fluids intersect at some point in the shearing gap. At this point, designated y<sup>\*</sup>, the Newtonian shear rate profile Eqn (6-12) can be used to calculate  $\dot{\gamma}_{ACT}$ 

(because at this point,  $\dot{\gamma}_{ACT} = \dot{\gamma}_N$ ). The stress profile Eqn (6-10), which is valid for all fluids, can be used to find the stress at y<sup>\*</sup>, and the viscosity can be calculated using  $\eta \equiv \sigma/\dot{\gamma}$ 

$$\eta(y^*) = \frac{\sigma_W - \frac{\Delta P}{L} y^*}{\frac{V}{h} \left( \frac{\sigma_W L - \Delta P y^*}{\sigma_W L - \Delta P \frac{h}{2}} \right)} = \frac{\sigma_W - \Delta P \frac{h}{2}}{\frac{V}{h}}$$
(6-14)

This gives the same result as the Newtonian viscosity equation (6-13) used to calculate the apparent viscosity. In effect, this method corrects the shear rate to match the apparent viscosity, so that at the point  $y^*$ ,  $\eta_N(\dot{\gamma}_N) = \eta_{ACT}(\dot{\gamma}_{ACT})$ . In fact, both  $\sigma_W$  and  $\dot{\gamma}$ are shifted, but the shift is cancelled out when calculating the viscosity, and only the shear rate is changed.



Figure 6-7 Shear rate profiles in the rheometer gap.

The key to this technique is the estimation of the shear rate profile intersection point, y<sup>\*</sup>. A power-law model,  $\sigma = m\gamma^n$  can be used to approximate the shear thinning fluid; Broadhead [12] found y<sup>\*</sup> to be relatively insensitive to variations in the power-law parameters for a range of polymers. In Figure 6-7, Newtonian and power law profiles are displayed. The power-law profile, taken from [44], is given by

$$\dot{\gamma}_{PL} = \left(\frac{n+1}{n}\right) \left(\frac{V}{h}\right) \left(\frac{\left(\beta - \frac{y}{h}\right)^{\frac{1}{n}}}{\beta^{\frac{n+1}{n}} - (\beta - 1)^{\frac{n+1}{n}}}\right)$$
(6-15)

where

(6-16) 
$$\left(\frac{\frac{n+1}{n}}{\beta^{\frac{n+1}{n}}-(\beta-1)^{\frac{n+1}{n}}}\right)^n = \left(\frac{\Delta Ph}{Lm}\right)\left(\frac{h}{V}\right)^n$$

must be solved numerically to find the value of  $\beta$ . The intersection points y<sup>\*</sup> for various shear rates, pressure drops and power law parameters are listed in Table 6-1. The position of y<sup>\*</sup> is not a strong function of strain rate or polymer viscosity and seems to

**Table 6-1** Table of y<sup>\*</sup> values calculated for high and low viscosity polypropylene at high and low shear rates and flow rates.

Resin	∆Р МРа	γ1/s	y* mm	
Profax 6631	.25	10	.484	
Power Law Coeff.	.62	10	.459	
n=.56	.25	30	.484	
m=6153	.62	30	.457	
Profax PD701	.14	10	.485	
Power Law Coeff.	.40	10	.456	
n=.625	.14	30	.492	
m=2775	.40	30	.478	

96

depend mainly on  $\Delta P$ . The mean value used for process measurements in this work, with a 95% confidence interval, was  $y^* = .474 \pm .01$  mm. The largest error in shear rate incurred in using the average value is 1% (for high  $\Delta P$ , low shear rate experiments). Measurements at higher shear rates are less affected by the value of  $y^*$  because the ratio of drag flow to pressure flow is much higher.

In order to examine how well the power-law shear rate profile modelled the polymer flow in the gap, a numerical scheme was developed to determine  $y^*$  for an arbitrary  $\sigma(\gamma)$  relationship. Given the speed of the moving wall, V, the pressure drop,  $\Delta P$ , and a stress-strain rate relationship, the procedure is as follows:

- 1) Assume a value for  $\sigma_w$ , and use eqn (6-10) to determine the stress profile  $\sigma(y)$  across the gap.
- 2) Invert the  $\sigma(\gamma)$  function to obtain  $\dot{\gamma}(\sigma)$ , and use this with  $\sigma(y)$  from (1) to determine the shear rate profile  $\dot{\gamma}(y)$ .
- 3) Integrate  $\dot{\gamma}(y)$  across the gap ( $\dot{\gamma}=\partial v/\partial y$ ) to get the velocity profile, and determine the moving wall speed V'.
- 4) Compare V' with V, update the wall stress estimate, and iterate through steps
  (1) to (4) until V'=V.

The MATLAB procedure FZERO, which finds a zero root for functions of a single variable, was used to find the value of  $\sigma_w$  that gave V'-V=0.

The numerical method was tested using a power-law model and was found to be in good agreement with the analytical solution described earlier. Then a cubic spline was used to fit actual stress-strain rate data to a curve, and this model was tested against the power-law results. In Figure 6-7, it can be seen that the profile calculated using the actual viscosity curve matches very well the power-law solution.

# 6.3 Temperature Compensation

Viscosity is a strong function of temperature; whenever a viscosity is reported, the temperature of the sample must be specified as well. The ILR does not control the process melt temperature, so it is not possible to set the temperature of the melt in the gap; a temperature correction algorithm is therefore needed to adjust the reported viscosity to a reference temperature. To do this, however, an accurate measurement of the sample temperature must be made.

The shearing gap is only 1 mm in height. It is very difficult to measure temperature in gaps this small. One is never certain if it is the polymer or wall temperature that is being measured. Also, the temperature distribution across the gap must be considered; this should be as uniform as possible. Broadhead attempted gap temperature measurements using a ribbon thermocouple but could not get reliable results. Using a variable depth melt thermocouple, he also measured the temperature distribution inside the rheometer. Even when the centre flow was 40°C higher than the wall temperature, it was found that the polymer within 3 mm of the wall was only 2 to 3°C warmer than the wall. He then simulated the heat balance in the gap, using steady state equations and considering conduction, forced convection and viscous heating effects. Below  $\dot{\gamma}=15$  1/s, it was found that polymer 2 to 3°C warmer than the gap walls has time to equilibrate with the wall temperatures. At higher shear rates, convection due to drag flow becomes important, and the temperature profile in the gap are reasonably close to the gap wall temperatures.

Another problem was the temperature of the rotating drum. It could not be measured on-line (an RTD was used while the drum was stationary) and could not be directly controlled. The drum was heated by the polymer and was often at a temperature slightly different from that of the rheometer body. Since all experiments were run with the same extruder temperature profile, the same screw speed and the same total throughput, the major source of melt temperature variation was variation in the viscosity, since this changes the amount of viscous heating in the extruder. At the highest viscosity (0% peroxide), the melt temperature in the rheometer was 229°C. Polymer at this temperature caused the rheometer to run at 209°C with no input from its heaters. Even if the setpoint temperature was lower, the rheometer had no cooling system to remove excess heat. The rheometer was therefore set to 209°C so that it would remain at a constant temperature over the entire viscosity range of interest. The drum temperature was then measured at various viscosities. For 0% peroxide (1125 Pas at 30 i/s), the drum temperature was found to be 211°C. At low viscosities (below 650 Pas at 30 1/s) the drum temperature dropped to 208°C. Assuming the wall temperatures to be equal and using the rheometer body temperature as the gap temperature introduces an error of  $\pm 2^{\circ}$ C over the entire viscosity range.

An Arrhenius type equation,

$$\eta(T_{REF}) = \eta(T)e^{\frac{E_A}{R}\left(\frac{1}{T_{REF}} - \frac{1}{T}\right)}$$
 (6-17)

where T is the temperature of measurement and  $T_{REF}$  is the reference temperature (both in Kelvin), was used to correct viscosity values to the reference temperature. The value of  $E_A$  for this polypropylene was determined experimentally on the sliding plate rheometer to be 27.1 kJ/mol at a temperature of 200°C. Using this value of  $E_A$ , the temperature uncertainty in the gap causes an uncertainty in the viscosity measurement of  $\pm 3\%$ . This is a systematic error and will only cause viscosity readings to drift after a disturbance in the temperature equilibrium (i.e. a large change in viscosity that significantly changes the amount of viscous heating in the extruder).

During a viscosity measurement cycle, the rheometer, after flushing the gap, allows the sample to relax for 3 s and then performs a baseline measurement for another 2 to 3 s. This 5 to 6 s pause allows the polymer in the gap to become conditioned to the gap wall temperature. The relaxation period in the cycle, during which the drum is stationary reduces the non-uniformity of the temperature profile prior to a viscosity measurement.

## 6.4 Techniques to Improve Sample Renewal

The dynamic response of the rheometer to a change in viscosity can be separated into two parts: pure transportation delay, or the time required for polymer to flow through the extruder to the rheometer, and the transient response of the rheometer itself, i.e. the time required for new material to purge old from the shearing gap. In the case of a step change in viscosity, the indicated viscosity approaches the new viscosity level asymptotically as new material replaces old in the gap during several measurement cycles.



Figure 6-8 Finite element simulation of flow through the process rheometer. Drum rotation is clockwise, polymer flow is from left to right. Figure from Broadhead [12].

To better understand this material replacement process, Broadhead [12] used a finite element simulation to examine flow patterns in the rheometer. He assumed a 2-D geometry and inertialess, isothermal flow of power-law fluid (n=.92 and .45). The simulation predicted that the polymer drawn into the gap is the slow moving polymer close to the wall. This increases the response time but helps with the temperature control, since the polymer near the wall is close to the wall temperature. The simulation also predicted large recirculation zones near the entrance and exit of the shearing gap, which worsen when the shearing drum is rotated in the forward direction. (For the



Figure 6-9 Finite element simulation of flow through the process rheometer. Drum rotation is counter-clockwise, polymer flows from left to right. Figure from Broadhead [12].

purposes of this study, "forward" rotation of the drum causes shearing in the same direction as the pressure flow, as indicated in Figure 6-8). The recirculation zones become smaller with increasing flow rate but never disappear entirely. These zones hold up material in the rheometer, increasing the breadth of the residence time distribution. They also greatly retard the introduction of new material into the shearing gap, increasing the response time of the rheometer. When the simulations were run with the direction of drum rotation reversed, the recirculation zones disappeared completely, and polymer flowed straight to the shearing gap. No streamlines actually passed through the gap, however, indicating no sample renewal was occurring at all. Fortunately, the 3-dimensional flow in the actual rheometer is more complex than that of the 2-D simulation, and experimental sample renewal was found to be much better than that predicted by the simulation.

A way to improve sampling is to use both forward and backward drum rotations alternately to flush the shearing gap. The backward rotation temporarily eliminates the recirculation zones and eases the flow of polymer through the rheometer. Once the main rheometer cavity has been flushed, forward rotation is used to draw new material into the gap. Even if recirculation occurs, the polymer in the rheometer is fresh and the shearing gap will receive new material.

**Table 6-2** Comparison of ILR response times to step changes in peroxide concentration using forward rotation shearing gap flushing with response times for backward/forward technique. (Steps: 100 - 200 ppm and 300 - 400 ppm peroxide.)

		Forwa	d Flush	Backward Flush		
Viscosity Levels	Step	t <sub>a</sub>	$ au_{ m p}$	ta	$ au_{p}$	
High $\eta$ (900 Pa·s)	Up	41 s	40 s	42 s	35 s	
$\Delta \eta = 120$ Pa·s	Down	41 s	71 s	41 s	29 s	
Low η (700 Pa·s)	Up	48 s	50 s	43 s	26 s	
$\Delta \eta = 75$ Pas	Down	44 s	70 s	49 s	31 s	

To accomplish this in practice, relays activated by the control computer were used to reverse the polarity of the field current in the rheometer drive motor (section 2.4.2). This allowed software control of the direction of the shearing drum. Experiments at various viscosity levels were performed to see if backward flushing significantly improved the response time of the rheometer to a step change in viscosity. In a 15 s measurement cycle, 7 s were used to renew the polymer in the gap. In one case, the drum was rotated forward at  $\dot{\gamma}$ =30 1/s for the entire period; in the second case, the drum was rotated backwards for the first 4 s and forwards for the last 3 s, flushing first the rheometer and then the gap. Some typical results are shown in Table 6-2, where t<sub>4</sub> is the dead time, or the amount of time before the rheometer starts to react, and  $\tau_p$  is the first order time constant of the rheometer response (see section 7.1.2).

The backward flushing technique offers several advantages over the use of the forward rotation only. No change in the amount of pure dead time was noticed. However, a large decrease in  $\tau_p$  was evident for the backward flushing runs, especially for the downward steps in viscosity. This brought the magnitudes of  $\tau_p$  for up and down steps closer together, reducing the non-linearity (see section 7.1) in the overall process response. The increased speed and linearity of the response reduce the amount of lag and distortion that the rheometer adds to the true (extruder only) process response.

#### 6.5 Elements of a Rheometer Measuring Cycle

The rheometer is designed to perform discrete measurements at regular intervals rather than give a continuous viscosity reading. This is due to the need to purge the shearing gap to get new polymer and to determine the baseline (zero shear rate) for each measurement. When the rheometer was used for process identification experiments, the cycles were kept short to collect as much information as possible.

A measurement cycle is made up of the following steps:

- Relaxation the polymer in the shearing gap is allowed to relax for several seconds with no drum rotation before the baseline reading is recorded. The polymer temperature also equilibrates to the wall temperatures.
- ii) Baseline Measurement the baseline stress and pressure readings are read by the control computer at 20 Hz.
- iii) Viscosity measurement The drum rotates forward at the desired shear rate. While waiting for the stress transients to die out, the control computer interrogates the MACO 8000 to get the rheometer and melt temperature values. After steady state is achieved (about one second), the computer samples the stress, strain rate (tachometer) and pressure sensors at 20 Hz.

- iv) Rheometer flush The drum rotates backward at 30 1/s to clear the recirculation zones at the entrance and exit of the shearing gap, flushing new polymer through the stagnant zones in the rheometer.
- v) Shearing gap flush The drum rotates in the forward direction at 30 1/s to drag a new sample into the gap. The recirculation zones reform, but are now composed of fresh material, and the gap is flushed with new polymer. The polymer sample is allowed to relax in preparation for the next measurement.



Figure 6-10 Rheometer measuring cycles for identification and control experiments: a)  $\Delta t=15$  s and b)  $\Delta t=25$  s.

Most identification experiments used a cycle length of 15 s, divided as shown in Figure 6-10a. This was the shortest cycle possible that allowed for adequate sampling (including backwards flushing). A control period of 25 s, Figure 6-10b, was chosen for the minimum variance controller (see section 7.2, 8.3). Most of the increased cycle time was used to aid the polymer flow through the rheometer using the backward flushing, keeping the residence time distribution in the rheometer as narrow as possible.

## 6.6 Rheometer Accuracy and Precision

A comparison was made between viscosity measurements made with the ILR and several other instruments. Extrudate samples were taken from the visbreaking process at low and high peroxide levels while the ILR was performing measurements. These extrudates were analyzed using a sliding plate rheometer (SPR) [3], which also uses an SST to measure stress, and a high pressure capillary rheometer. The data are presented in Table 6-3.

Table 6-3 - Comparison of viscosity from ILR, SPR and capillary rheometers. The viscosities are listed in Pa-s, and are taken at 30 1/s, 209°C. Each result reported for the ILR is an average of 11 measurements, with the standard deviation listed as well.

ppm	ILR	Std Dev.	SPR	Capillary
100	1005	1.2%	1057	1099
150	933	1.1%	890	1024
350	696	2.1%	690	684
400	668	1.7%	663	667

The results listed for the ILR are an average of 11 measurements taken when the process was stable at the specified peroxide level (open loop operation). The standard deviations are also presented in Table 6-3, showing the repeatability of the instrument. Variations in the measurements can be attributed to process noise as well as rheometer precision. Large pressure fluctuations caused by surging in the extruder tended to raise the standard deviation slightly at the lower viscosities (see section 6.2.1).

The SPR was used to generate viscosity values using an instrument based on the same general principle as the ILR. Since both machines use an SST, the SPR should highlight effects of performing the measurement in-line. Note, however, that the SST used in the laboratory instrument was much stiffer than in the ILR; the measurements were made at the low end of the sensitivity of the instrument. The capillary rheometer, a Goettfert Rheograph 2002, was used to provide viscosity data typical of a more conventional machine. A 30/2 mm die was used for all testing. No Bagley corrections were made because there was insufficient sample for multiple runs; this will cause the measurements to be slightly high for this instrument. Visbroken polypropylene, however,

with its narrow MWD, should have only a small entrance pressure correction. Measurements in the SPR and the capillary rheometer were performed at the same temperature as the process rheometer setpoint, 209°C.

Agreement between the three machines is generally good, especially at the higher peroxide concentrations. At higher viscosities, viscous heating of the polymer in the extruder causes higher temperatures and larger temperature gradients in the rheometer. The temperature of the melt drawn into the measurement zone rises as the viscosity increases, causing a reduction in the measured stress (see section 6.3) and a viscosity value slightly lower than expected.

Broadhead [12] performed an extensive comparison of viscosities measured with the ILR with viscosities measured in the SPR. He used a number of resins besides the ionomers that were the focus of his studies, including the base polypropylene (Profax 6631) used in this study. He also found good agreement between the two machines over the entire ILR shear rate range for polypropylene, though there was some scatter in the data at low shear rates. This is because the relative size of stresses due to pressure fluctuations are on the same order of magnitude as the stress due to the rotating drum. Overall, the ILR agrees quite well with the viscosity data from other instruments.

Û

#### CHAPTER 7

# PROCESS IDENTIFICATION WITH THE IN-LINE RHEOMETER

Before closed loop control can be applied to the visbreaking process, one must determine the static and dynamic responses of the controlled variable, viscosity, to changes in the manipulated variable, peroxide concentration in the feed. Models must be developed for use in simulations to predict optimum PI tuning parameters, and for incorporation directly into controllers such as the minimum variance type. Also, previous studies [10,45] how that the polypropylene visbreaking process is nonlinear both in symmetry (the shape of the step up versus step down response) and in gain. Deterministic and stochastic identification methods were used to determine models of the process dynamics at a fixed feed rate, 12 kg/h. The fraction of the total system response due to the response of the rheometer is also examined.

The extruder temperature zones were set to 180°C (feed zone), 190°C, 200°C and 200°C respectively, while the rheometer temperature was held at 209°C (as explained in section 6.3). Screw speed was kept constant at 300 RPM, and a vacuum was applied to the devolatilization port.

## 7.1 Continuous Time Modelling

#### 7.1.1 Steady State Control Charts

Steady state control charts show the controlled variable as a function of the manipulated variable at steady state. They are used to find reasonable operating ranges and to inform the operator of which steady state viscosity to expect when doing dynamic experiments. In the present study, the control chart was also used to select the rheometer shear rate,  $\dot{\gamma}$ , used in viscosity measurements. Figure 7-1 shows the sensitivity of the viscosity to the concentration of peroxide at several shear rates. The slope of the control graph is the process gain  $k_p$ ; this value increases as  $\dot{\gamma}$  decreases. The nonlinearity of the gain with respect to peroxide concentration is also visible, as the magnitude of the viscosity-peroxide concentration slope is reduced at higher peroxide concentration levels.



Figure 7-1 - Control graph for visbreaking process, with  $\eta$  measured at 3 different shear rates

There are no measurements for peroxide concentrations less than 100 ppm as this was the minimum stable feed rate obtainable from the masterbatch feeder. At 12 kg/h, using masterbatch A (1000 ppm peroxide) to prepare the control graphs, the minimum stable extrudate concentration was 125 ppm peroxide. Masterbatch B (500 ppm peroxide) was used in later experiments to reduce this limit to 60 ppm.

γ k<sub>o</sub>/S.D. S.D. k, 10 1/s 41 Pars -2.6 Pa-s/ppm .063 -1.4 Pa-s/ppm 25 1/s 17.4 Pa-s .080 30 1/s 15.3 Pa-s -1.2 Pa·s/ppm .079

Table 7-1 - Average standard deviations,  $k_p$  (from best linear fit) and ratios for data in Figure 7-1

Unfortunately, as  $\gamma$  decreases, the standard deviation (S.D.) of the viscosity measurements increases, due mainly to pressure flow effects that become more significant relative to the reduced stress levels at lower shear rates. The optimum shear rate is the one having the best k<sub>p</sub>/S.D. ratio. In Table 7-1, we see that the ratios for  $\dot{\gamma}=25$  1/s and  $\dot{\gamma}=30$  1/s are more or less the same; later experiments showed  $\dot{\gamma}=30$  1/s to be slightly superior, particularly after some improvements in the pressure compensation algorithm (see section 6.2.1).

The control graph for  $\dot{\gamma}=30$  1/s, with error bars corresponding to 1 S.D., is



Figure 7-2 - Control graph, viscosity verses peroxide concentration, with single standard deviation error bars

displayed in Figure 7-2. Surging problems encountered around 700 Pas were manifested as higher standard deviations for viscosity measurements in that region. The range of interest for control purposes was chosen to be between 100 and 400 ppm peroxide. The response is reasonably linear, as shown by the linear fit through the points in that region, and a reasonable range of viscosity is covered.

#### 7.1.2 First Order with Dead Time Models

The easiest and quickest method of examining the dynamics of the process viscosity response to a change in the feed peroxide concentration was to perform deterministic step tests. Examining the shapes of the responses gave a rough idea of the



Figure 7-3 - Response of the visbreaking process to step changes in the peroxide concentration,  $\dot{\gamma}=30$  1/s.

order of the response, as well as estimates of model parameters. The response of the visbreaking system to changes in the peroxide concentration is shown in Figure 7-3. The roughly exponential curves, with no overshoots or other signs of higher order dynamics, suggested that a first order model could be used. The appreciable lag between the time of the disturbance and the start of the response suggest that a dead time parameter should also be incorporated into the model. The first order with dead time model is:

$$\Delta \eta(t) = \Delta U \cdot k_p \left( 1 - e^{\frac{-(t-t_d)}{\tau_p}} \right)$$
(7-1)

where  $\Delta u$  is the magnitude of the step change in peroxide concentration;  $k_p$  is the process gain, which controls the magnitude of the change in viscosity;  $\tau_p$  is the process time constant, which reflects how quickly the system changes; and  $t_d$  is the dead time, or the delay until the process starts to change.  $\Delta \eta(t)$  is the change in viscosity as a function of time.

A fitting routine was written (using MATLAB, V3.5, with the multi-variable minimization routine FMINS) to find the best fit of the parameters to the step test data. While  $k_p$  is specified by the initial and final steady state viscosities,  $\tau_p$  and  $t_d$  are correlated and can be difficult to determine. In Figure 7-4, for a large change in



Figure 7-4 - A 175 ppm step down in peroxide concentration, with a fitted first order plus dead time model

concentration, the model has no trouble fitting the parameters; the signal to noise ratio is manageable and the starting point of the response is clear. Unfortunately, the response of the system to large changes in viscosity tends to be nonlinear, due both to the changing  $k_p$  and the asymmetry between large up and down steps (see Figure 7-3, where the response of the initial large downward step is slower than that of the large upward step near the end of the experiment). This asymmetry is attributed to flushing effects in the rheometer and extruder; where there is a large difference in viscosity, high viscosity polymer will flush out lower viscosity polymer faster than vice-versa [42]. Small peroxide concentration changes, while less susceptible to flushing effects because of the small change in viscosity, are hidden by the noise, and it becomes very difficult to establish when the system starts responding (see Figure 7-5).



Figure 7-5 - Small change in peroxide concentration, fitted with first order plus dead time model. Noise makes it difficult to determine exactly how much of the response is dead time  $(t_d)$ .

Another limitation in the accuracy of the modelling is the sampling rate; the fastest cycle time for the rheometer is approximately 15 seconds. This is a large fraction of the process time constant experienced with this system. Ideally, a maximum sampling period of 1/10 of the process time constant is required for good resolution [46]. This is about one third of the current minimum cycle time.

A number of experiments were performed to evaluate the repeatability of the deterministic step tests. The results from a typical set of runs are listed in Table 7-2. It can be seen that while the gain and dead time parameters are consistent enough to yield some information, the process time constants fluctuate wildly and are not repeatable. Problems with measurement noise (i.e. noise due to the rheometer), process noise (such as variations in the polypropylene feedstock and imperfect dispersion of the peroxide in the masterbatch) and the low sampling rate combine to limit the usefulness of deterministic identification methods. Stochastic methods give better results because they can model process noise.

CONC STEP (ppm)	k <sub>p</sub> (Pa-s/ppm)	τ <sub>p</sub> (s)	t <sub>a</sub> (s)
100 to 150	-1.19	5.0	51.8
100 to 150	-1.19	68.1	51.8
150 to 100	-1.41	38.4	41.5
150 to 100	-1.21	18.9	46.2
100 to 125	-1.04	0.3	59.1
100 to 125	-1.23	27.2	43.1
125 to 100	-0.91	5.8	51.8
125 to 100	· -1.45	71.0	45.3
125 to 150	-1.27	77.8	51.8
125 to 150	-1.17	43.6	46.2
150 to 125	-1.01	55.2	51.8
150 to 125	-1.11	50.1	67.6

**Table 7-2** - Model parameters for the first order model (7-1) calculated for a series of step tests.

# 7.2 Discrete System Modelling

Stochastic methods of process identification use statistical techniques to separate noise from process dynamics. A pseudo-random binary signal (PRBS) was used as an input signal to excite the process under study. Since the PRBS consists of a large number of positive and negative steps between two concentrations, rather than just a single step, the output signal contains much more information than in the deterministic case. Correlative techniques are used to determine which part of the response can be attributed to the process, which is assumed to be linear. The rest of the signal, including any nonlinearities, is considered noise. This noise (provided that it is not completely random) can also be modelled, and will provide information useful for designing a suitable minimum variance controller.

2

Once the experimental results (u(t), which was a PRBS sequence, and the resulting  $\eta(t)$  measured by the rheometer) were available, several steps were needed to determine the best model. First, the structure of the model was established. This involved determining the number of whole periods of dead time, the order of (or number of parameters in) the process model and the order of the noise model. Parameter values were then fitted using MATLAB routines to a number of likely model structures (i.e. a first order model with one gain term, a first order model with two gain terms, different numbers of dead time periods, etc.). The model with the best compromise between complexity and fit was then chosen to describe the data (see Appendix A).

The best process model (noise models will be discussed in section 7.2.2) was found to be first order with two gain parameters, shown as Eqn (7-2). MATLAB V3.5, together with its Control and System Identification "toolboxes", was the software used for data analysis. Two routines were of particular interest in this case. The OUTPUT ERROR routine ("OE") calculated only process model parameters while attempting to minimize the effects of noise. The BOX-JENKINS routine ("BJ") estimated parameters for the process model and the noise model at the same time. Both routines returned estimated standard deviations for the calculated parameters. A detailed analysis of a PRBS identification run is presented in Appendix A. In general, the simpler OE model was fit first, with no noise model. If analysis of the residuals indicated the presence of correlated noise, then the BJ model was used; otherwise, the results of the OE model were reported.

## 7.2.1 First Order Models with Dead Time

A continuous first order model with dead time, as defined in (7-1), may be rendered into discrete form as follows [49]:

$$(1 - \delta z^{-1})\eta_t = (\omega_0 + \omega_1 z^{-1})u_{t-f-1}$$
(7-2)

where 
$$\delta = \exp(-\Delta t/\tau_p)$$

$$\begin{split} \omega_0 &= k_p (1-\delta^{1-c}) \\ \omega_1 &= -k_p (\delta-\delta^{1-c}) \\ \Delta t &= \text{ sampling period} \\ f &= \text{ number of whole periods of dead time} \\ c &= \text{ fractional period of dead time, so that } t_d &= (f+c)\Delta t \\ z^{-1} &= \text{ backwards shift operator} \end{split}$$

Translating the discrete results to the continuous time domain format allows comparison with parameters obtained from deterministic tests, as well as between discrete tests using different sampling periods. Using two parameters for the gain,  $\omega_0$  and  $\omega_1$ , allows the modelling of fractional periods of dead time. Models with this structure, however, may become non-invertible if the fractional period c becomes too large and if the absolute value of  $\omega_1$  becomes larger than that of  $\omega_0$ . Minimum variance controllers use the process model in inverted form (i.e. numerator and denominator are interchanged). A model is non-invertible if it becomes unstable when inverted. Proper selection of the sampling period,  $\Delta t$ , will avoid this problem.

Typical data from an identification run are presented in Figure 7-6. A PRBS waveform generated the input peroxide concentration setpoints, which stepped between 100 and 150 ppm, and the viscosity response was monitored at 15 second intervals. Deterministic step tests showed that large steps are asymmetrical in shape (Figure 7-3). The PRBS test steps were much smaller in size and caused only small perturbations in the viscosity ( $\pm 25$  Pa s in Figure 7-6). For these small disturbances, the viscosity response was assumed to be symmetrical, with the same shape in the up and down

2.5



Figure 7-6 - Data from a stochastic identification experiment. The input concentration setpoints are the PRBS waveform in the lower graph, while the upper shows the process response.

directions. The process gain,  $k_p$ , was also assumed constant over the range of the PRBS test, so that the process could be considered linear.

RUN #	ω	$\omega_1$	δ
1	111±.04	454±.04	.310±.06
2	$192 \pm .04$	$432 \pm .05$	.456±.04
3	$172 \pm .02$	$466 \pm .02$	$.301 \pm .04$

Table 7-3 - Results from replicate PRBS runs, with  $\Delta t=15$  s, concentration midpoint 125 ppm and a step size of 50 ppm. Parameters are calculated using two full periods of dead time and listed  $\pm$  one standard deviation.

A number of experiments with the same process parameters were carried out to examine the consistency of the PRBS method. Table 7-3 summarizes the results. The values of the gain parameters,  $\omega_0$  and  $\omega_1$ , are all within a single standard deviation of their average, indicating that (at least within this particular batch) the feedstock is homogeneous. The average calculated value of  $k_p = -0.961$ , where

$$k_p = \frac{\omega_0 + \omega_1}{1 - \delta} \tag{7-3}$$

This is close to the values obtained from deterministic tests performed in the same region. The  $\delta$  parameter, which is related to the process time constant, has slightly more variability, indicating that the positive and negative responses are not exactly symmetrical as was assumed. As well, the average value of  $\tau_p$  is 14.5 s, which is the same order of magnitude as the  $\Delta t$  used for the tests. A faster rheometer measuring cycle is needed to decrease  $\Delta t$  and increase the resolution and accuracy of the identification experiments. The average  $t_d$  is 57.3 s, again as expected from previous tests. Run 3 was twice the length of runs 1 and 2, resulting in lower standard deviation values for that run. The consistency of the stochastic tests here is obviously much better than that of the deterministic step tests in section 7.1.2.

Table 7-4 - Parameters from runs with varying step size,  $\Delta t=15$  s, concentration midpoint 125 ppm. Analyzed using two full periods of dead time, parameters shown with  $\pm$  one standard deviation.

Step Size	ωο	$\omega_1$	δ
30 ppm	$242 \pm .05$	$372 \pm .08$	.432±.07
50 ppm	$211 \pm .03$	$389 \pm .04$	$.357 \pm .05$
50 ppm	$228 \pm .03$	$358 \pm .05$	$.442 \pm .04$
50 ppm	153±.03	$457 \pm .03$	.362±.04

To check the linearity assumption, tests were run about the same peroxide setpoint using different size peroxide steps. This should show if there is any dependence of the model parameters on step size. Results are listed in Table 7-4.

The gain parameters were within one S.D. except for the 70 ppm step run, which gave a slightly longer dead time than the others; this resulted in the difference in the  $\omega_0/\omega_1$ ratio for this run compared with the others. Again, the  $\delta$  values were not as repeatable as the gain parameters, but there was no pattern to the scatter. Increasing the step size seemed to decrease the standard deviation of the parameters due to a better signal to noise ratio, but had no discernable effect on the value of the parameters.

The length of the sampling period,  $\Delta t$ , affects the model parameters because it changes the structure of the model. The number of whole periods of dead time, **f**, might change, as well as the size of the fractional period **c**. The length of the rheometer cycle also governs the degree of flushing in the rheometer before taking a measurement. Longer cycles permit more flushing, which should improve response of the rheometer due to faster sample renewal.

In Table 7-5, the results of experiments run with three different viscosity sampling rates are reported. For sampling periods of 15 s, dead times of 55 - 60 s were calculated from the data in Table 7-4 using Eqn (7-2). When  $\Delta t$  was decreased to 13 s or increased to 25 s, calculated dead times on the order of 60 - 63 s were noted. The increase in the t<sub>d</sub> parameter, when one would expect better flushing and faster response for  $\Delta t$ =25 s, is attributed to the fact that the process response is only approximately first order. Different  $\Delta t$  values cause the model to fit differently. The viscosity response appears to start faster than an exponential, but has a long tail before reaching steady state. This suggests that the response might be more precisely modelled as two first order processes in parallel.

The decrease in time resolution for a 25 second cycle ( $\Delta t$  is now approximately twice  $\tau_p$ ) also hampered attempts to accurately determine  $\tau_p$  (and  $t_d$ , since these parameters are related). For low viscosity experiments at  $\Delta t=25$  s, the parameter fitting routines could not find a reasonable value for  $\delta$ . The lower process gain in this region caused smaller process responses, decreasing the resolution of the rheometer. For these

Δt s	η Pa-s	u ppm	ω <sub>0</sub>	$\omega_1$	δ	k <sub>p</sub>	τ <sub>p</sub> S	t <sub>d</sub> s
13	978	125	33 ±.02	31 ±.03	.37 ±.04	-1.0	13	60
f=4	819	250	14 ±.02	32 ±.02	.41 ±.04	77	14	62
	660	375	07 ±.02	28 ±.02	.42 ±.06	60	15	63
15	961	125	25 ±.02	45 ±.03	.34 ±.04	-1.1	14	56
f=3	671	375	1 ±.05	24 ±.06	.51 ±.09	71	22	56
25	892	150	43 ±.03	26 ±.05	.21 ±.09	86	16	64
f=2	783	250	35 ±.03	20 ±.04	.22 ±.1	72	17	64
	655	375	19 ±.03	16 ±.03	.23*	45	17	66

Table 7-5 Results of experiments conducted with different  $\Delta t$  values. f, the number of periods of dead time, is listed with  $\Delta t$ .

\*: This value could not be determined using modelling techniques, but was estimated from previous experiments.

experiments,  $\delta$  was fixed at an average value calculated from experiments at higher viscosities. The modelling routines were able to assign reasonable values to the other parameters ( $\omega_0$ ,  $\omega_1$ , and  $\theta$ ) once  $\delta$  had been fixed.

For a discrete model to be useful for a minimum variance controller, it must be invertible. The sampling period,  $\Delta t$ , should be chosen so that a small positive value for the fractional dead time, c, results, and  $|\omega_0| > |\omega_1|$ . Table 7-3 and Table 7-4 show that  $|\omega_1|$  is, in all cases, considerably larger than  $|\omega_0|$ , so that while these models accurately describe the process, they are non-invertible. Models determined from data for  $\Delta t=25$  s, shown in Table 7-5, are all invertible.

The main effect of viscosity on the process model is to alter the value of the steady state gain,  $k_p$ . Based on the results of early, exploratory experiments, the gain  $k_p$ 



Figure 7-7 - Process gain  $k_p$  as a function of viscosity. Results are compiled from PRBS tests at  $\Delta t = 13$ , 15 and 25 s.

was assumed to be approximately linear with viscosity. As can be seen in Figure 7-7, more complete results confirmed this assumption. Using the continuous model parameter  $k_p$  to represent the gain allows data from discrete tests with different  $\Delta t$  values to be included in the computation. The probable cause for the variable process gain, due to stabilizer added to the base polypropylene resin, is discussed in section 3.4.

Another trend, although insufficient data were available to quantify it, was an increase in the dead time as viscosity decreased. For each  $\Delta t$  used (13,15 and 25 s), the t<sub>d</sub> parameter calculated for lower mean viscosity values ( $\approx 660$  Pa·s) was 2 to 3 seconds greater than at high viscosity (>900 Pa·s). Neither the pumping action of the extruder nor the drag flow flushing of the gap in the rheometer move material as effectively at lower viscosities. This would tend to slow the rheometer response, so the increase in t<sub>d</sub> is thought to be a real effect of the process, as opposed to an artifact of the modelling process.

In conclusion, a discrete model incorporating first order process dynamics and fractional period dead times was found to adequately model the visbreaking process using the in-line rheometer as the control sensor. The major nonlinearity identified was in the process gain, which varied linearly with viscosity. The asymmetry of the viscosity response to positive and negative concentration steps is negligible for the small steps of the PRBS tests. The PRBS tests themselves were able to give much more reliable results than the deterministic step tests first tried. They are capable of disregarding much of the noise present in the viscosity signal.

## 7.2.2 Process Noise Model

Stochastic modelling techniques provide noise models as well as process response models. Minimum variance controllers use these models to optimize their response to process disturbances. Typical disturbances in this process are due to feeder, temperature or masterbatch concentration fluctuations. Note that these disturbances must be present in the process during a PRBS test to provide data for the noise model, so that the controller can be optimized for these specific disturbances.

Another source of noise is the non-homogeneity of the polypropylene feed resin, with different bags of polymer having slightly different molecular weight distributions. Also, variations in stabilizer concentration will affect how much of the peroxide reacts with the polypropylene. This suggests that an integrating noise model should be employed. (An integrating noise model is one that results in integrating control action when used in a minimum variance controller, to correct long term drifts in the viscosity.) Experimentation with various noise model structures showed that a first order moving average integrating model was sufficient to model the disturbances encountered in the visbreaking process. This model has been studied by Palmor and Shinnar [47], who found it to be a good approximation for many processes. This model has the form

$$N_t = \frac{1 - \theta z^{-1}}{1 - z^{-1}} a_t$$
 (7-4)

# where $N_t$ is the noise at time t $\theta$ is the model parameter $a_t$ is a white noise signal, zero mean, unit S.D. $z^{-1}$ is the backwards shift operator

As the viscosity level varies more due to larger random disturbances, the value of  $\theta$  will increase, reducing the magnitude of the 1- $\theta$  term so that the current viscosity,  $\eta_t$ , is less dependent on the previous viscosity,  $\eta_{t-1}$ . In a minimum variance controller,  $\theta$  acts as a filter on the controlled variable. The larger the value of  $\theta$ , the slower the controller will react to shifts in the mean level of  $\eta$ , since the 1- $\theta$  term more heavily filters the viscosity data entering the controller.

The value of  $\theta$  is strongly dependent on the sampling period,  $\Delta t$ . For  $\Delta t=15$  s,  $\theta$  varied from 1 to 0.7, depending on the amount of noise in the system. For  $\Delta t=25$  s, results varied from  $\theta=0.7$  for slight shifts to 0.3 for large amounts of injected noise. In all cases, a relatively large standard deviation of 0.1 was recorded, indicating that these  $\theta$  values are only approximate. A value of  $\theta=0.65$  was initially selected to represent the process operating under normal circumstances, with  $\Delta t=25$  s.  $\theta$  was later varied to determine its effect on controller responses to disturbances and setpoint tracking.

## 7.3 Rheometer Dynamics

Using the process models developed in this chapter, and the residence time distribution data collected by Chen [48], it is possible to estimate the component of the process response due to the rheometer. The major sources of delay in the process signal are the feeder response, the residence time in the extruder, the time to reach the point of measurement in the rheometer, and the time for the rotating drum to draw a new sample into the shearing gap.

The feeders respond to setpoint changes quickly, with a time constant somewhat less than 5 s. The feeders were observed to take 10 to 15 s to settle to a new feed rate, depending on the size of the rate change.

Figure 7-8 demonstrates how the presence of the rheometer changes the residence time of the overall system at a throughput of 12 kg/h. The polymer used by Chen for the RTD studies was the same polypropylene that was used in this work. The RTD is



Figure 7-8 - Residence time distribution for extruder with and without the rheometer. Data from Chen [48]

much broader when the rheometer is installed. This is attributed to the volume and geometry of the rheometer cavity. Twelve seconds of pure time delay are added, and the mean residence time almost doubles. These measurements, made at the exit of the die, are not directly related to the time taken for polymer to reach the rotating drum in the rheometer. The point of measurement is approximately half way between the exit of the extruder and the exit of the rheometer; the RTD for that point is assumed to be midway between the extremes in Figure 7-8. This suggests that the extruder has a pure time delay of 24 s, with an additional 6 seconds necessary for the melt to reach the measuring point.

The process identification experiments conducted for the high viscosity polypropylene (i.e. low peroxide concentrations) gave dead times between 55 and 60 s, increasing with decreasing viscosity. Approximately 45 s are required for the feeder response and melt transport to the extruder exit, leaving 10 to 15 s to flush the shearing

 $\sim$
gap with fresh polymer. This seems reasonable, since, according to Figure 7-8, the concentration of new polymer at the measuring point increases more gradually than the sharp pulse that exits the extruder. Sufficient amounts of the new polymer must be dragged into the shearing gap to make a measurable difference before the rheometer will begin to respond.

The greater width of the RTD in the rheometer will lead to larger values of the rheometer time constant, assuming a first order response. The PRBS tests, however, predict  $\tau_p$  values for the entire process to be on the order of 15 s; this is somewhat faster than the RTD data might indicate. The RTD data in Figure 7-8 were taken with the drum stationary. Flow simulations performed by Broadhead [12] indicate that recirculation zones are present, which would increase the breadth of the RTD. These zones disappear when the drum is rotated in a direction so its lower portion moves in the same direction as the main polymer flow. This reduces the RTD breadth and allows the rheometer to respond faster than when the drum is stationary. (See section 6.4)

The ILR, with a lag time of 6 s and time constant of less than 15 s, performs very well when compared with commercial process rheometers. Fritz and Stöhrer [10] used a Rheometrics On-line Rheometer to monitor the degradation of polypropylene in a ZSK-30. They reported both dead times and time constants on the order of 3 minutes, most of which was attributed to the rheometer. Curry and Jackson [25] used a Goettfert Capillary By-pass Rheometer to control the same process, reporting dead times of about 4 minutes. Goettfert has recently described a rheometer [8] which, when running polypropylene, recorded a process dead time of 1 min and a time constant of 2.3 min. This gives the rheometer a dead time roughly the same as the ILR, but a longer time constant. The exact extruder configuration used for the tests was not mentioned, so it is difficult to directly compare these instruments.

# 7.4 Identification Summary

A first order with dead time model was found to be adequate to model the effect of peroxide concentration on the polypropylene visbreaking process. Significant nonlinearities in both the process gain and symmetry of the process time constant were found. In order to minimize the effects of these nonlinearities, small steps in peroxide concentration had to be used to model process response characteristics. This led to the use of stochastic identification methods, since the response of a single, small step in concentration was obscured by process noise.

The process gain was found to be a function of shear rate as well as peroxide concentration. The best gain to process noise ratio was found to be at high shear rates; all modelling was performed at  $\dot{\gamma}=30$  1/s, at the high end of the rheometer's shear rate range. The process noise was modelled using a first order moving average integrating model. The full discrete first order plus dead time plus noise model that represents the process is

$$\eta(t) = \frac{\omega_0 + \omega_1 z^{-1}}{1 - \delta z^{-1}} u(t - f - 1) + \frac{1 - \theta z^{-1}}{1 - z^{-1}} a(t)$$
(7-5)

where  $\theta = 0.65$  and parameter values for  $\Delta t = 25$  s from Table 7-5 are used.

The fastest rheometer measuring cycle was 13 s, the same order of magnitude as the process time constant. This limited resolution hampered the ability of the modelling routines to determine the  $\delta$  parameter, the discrete equivalent of the first order time constant. This resulted in the  $\delta$  parameter having a larger standard deviation than the gain parameters  $\omega_0$  and  $\omega_1$ .

# CHAPTER 8 PROCESS CONTROL WITH THE IN-LINE RHEOMETER

Once process models had been determined, controllers were developed to close the control loop. The viscosity monitored by the ILR was used as a feedback signal to manipulate the level of peroxide in the extruder. A proportional plus integral controller was first implemented, using gain scheduling to improve performance at low viscosity. This was followed by a minimum variance controller, which included a dead time compensator to offset the long delay times present in this system. Gain scheduling was incorporated into this controller as well. Both controllers were tested for their response to setpoint changes and load disturbances.

#### 8.1 Proportional-Integral Controller

The first control algorithm employed was the standard PI (proportional plus integral) controller. Its use has been reported extensively in the literature [10,25,26], and it is easy to implement. It does not allow for dead time compensation, however, and had to be detuned because of the significant dead time present in this process.

A large amount of dead time can cause stability problems with PI controllers. When the controller makes a correction, the effect of the action may not appear at the process output before the controller is called upon to make another control action. As a result, it makes another, unnecessary, adjustment, swinging the process too far in the other direction. When the controller senses this error, it will overcorrect and the control loop will oscillate. To avoid this, the controller is detuned so that it implements only a fraction of the required control action during each control period and any oscillations will be damped out. It also makes the control loop behaviour sluggish, responding slowly to process disturbances and setpoint changes.

### 8.1.1\_PI\_Control Simulations

Simulations performed in MATLAB were used to find rough estimates for the controller parameters as outlined below. Fine tuning of the parameters and gain



Figure 8-1 Control diagram of the visbreaking process

scheduling were performed using the actual process. Figure 8-1 shows the block diagram for the process.  $G_{p}(s)$  is the first order plus dead time Laplace transfer function of the process (including the rheometer dynamics) as determined in chapter 7.

$$G_{p}(s) = \frac{k_{p} \cdot e^{-t_{d}s}}{\tau_{p}s + 1}$$
(8-1)

The process parameters derived from high viscosity experiments ( $k_p = -1$ ,  $\tau_p = 16$  s and  $t_d = 56$  s) were used to obtain controller parameters that would be stable over the entire control range. A tenth order Padé function was employed to approximate the dead time term e<sup>-td-s</sup>, since the MATLAB routines required that the numerator and denominator of the transfer function be in polynomial form. G<sub>C</sub> is the transfer function of the PI controller

$$G_{c}(s) = k_{c}\left(1 + \frac{1}{\tau_{I}s}\right)$$
 (8-2)

where  $\mathbf{k}_{c}$  is the controller gain and  $\tau_{I}$  is the integral time constant.  $G_{D}(s)$  represents any low frequency noise or load disturbances entering the system. For the servo problem

 $G_D(s)=0$ , and for the regulator problem,  $G_D(s)$  is the transfer function of the disturbance. Low frequency noise was assumed to enter the system mainly through the feeders (feed rate fluctuations, resin property fluctuations, etc.).  $\eta_{seept}(s)$  is the viscosity setpoint and  $\eta(s)$  is the viscosity output of the system.

For the servo problem (the response of the process to setpoint changes), the transfer function of the response in the continuous time domain is

$$\eta(s) = \frac{G_{p}(s) \ G_{C}(s)}{1 + G_{p}(s) \ G_{C}(s)} \cdot \eta_{sept}(s)$$
(8-3)

To find the tuned values for  $k_c$  and  $\tau_I$ , the response of the system to a unit step change in viscosity ( $\eta_{setpl}(s)=1/s$ ) was optimized; the response was repeatedly calculated, a cost



**Figure 8-2** Continuous time process simulation results; the optimal response of the process to a unit step in  $\eta_{sept}$  calculated using the three different error functions and compared with the open loop response

function was determined, and  $k_c$  and  $\tau_I$  were adjusted to minimize the value of the function. The MATLAB routine FMINS was used to perform the minimization. Three cost functions were examined: the integral of the squared error (ISE); the integral of the

absolute value of the error (IAE); and the integral of the time-weighted absolute error (ITAE), where the error is  $\eta_{sept}(t) - \eta(t)$ . ISE gave the fastest process response, with a large overshoot, while the ITAE function gave the fastest settling time but had a slow initial response. The IAE function was a compromise that fell between these extremes.

The open loop response shown in Figure 8-2 was faster than any of the simulated responses with a controller present. This does not mean that open loop control would be sufficient to control the process. The controller response delays were due to the large ratio of dead time to process time constant  $(t_d/\tau_p \approx 4)$ , called the controllability ratio by Fritz [10]. Fritz suggests that this ratio must be less than one in order to achieve good control. While the addition of a controller slowed the process response when compared with an open loop step, the nonlinearity of the process gain would make open loop control difficult. The integral action of the controller compensates for this. Also, as shown below, this controller provided automatic disturbance rejection functions to keep the process at constant viscosity.

**Table 8-1** Continuous time PI controller parameter results from control simulations using a first order plus dead time model ( $\tau_p = 16$  s,  $k_p = -1$ ,  $t_d = 56$  s)

	ITAE		IAE		ISE	
	k <sub>c</sub>	$ au_{ m I}$	k <sub>c</sub>	$\tau_{\rm I}$	kc	$\tau_1$
Servo	36	33 s	44	38 s	60	51 s
Regulator	41	36 s	47	40 s	66	53 s

The regulator problem, where the effects of a disturbance are modelled, was also examined. The regulator response transfer function is

$$\eta(s) = \frac{G_D(s) G_P(s)}{1 + G_P(s) G_C(s)}$$
(8-4)

where a unit step function,  $G_D(s)=1/s$ , was used as the disturbance. The results of both simulations are presented in Table 8-1, where it can be seen that the regulator problem generated slightly higher gains with less integral action for the same error function. The high controller gains give the ISE simulation its strong initial response, while the ITAE cost function gives parameters with a stronger integral action.

A PI controller has no dead time compensation, so  $\Delta t_c$  should be at least as large as  $t_d$ . Specifying too large a value, however, will make the controller sluggish.  $\Delta t_c = 75$ s was chosen, meaning the control period is approximately equivalent to  $t_d + \tau_p$ . This allows the process to respond to a control action before the next process measurement and control action are performed, increasing its stability.

#### 8.1.2 Experimental Results: Setpoint Tracking

The discrete PI controller was implemented in velocity form, which specifies a change in the manipulated variable rather than calculating its absolute value [49]. This prevents integral windup and makes the calculation of steady state values for initialization unnecessary. A control action was calculated as follows

$$\Delta u_t = k_C \left( 1 + \frac{\Delta t_c}{\tau_I} \right) e_t - k_C e_{t-1}$$
(8-5)

where  $\Delta u_t$  is the change in peroxide concentration for time t and  $e_t$  is the process error,  $\eta_{sept}$ - $\eta_t$ , at time t. The first term on the right is the control action for time t, while the second term removes the effect of the proportional action from the previous control period.

The IAE tuning parameters for the continuous time servo problem, which fell between the values calculated for the other error functions, were selected from Table 8-1 for the initial control run. Some care must be taken when transferring results from a continuous time controller to its discrete equivalent. Since the discrete controller receives feedback only periodically from the process, it will react to process changes more slowly and will not be as stable. In this case, the resulting controller was stable, but the process



Figure 8-3 Process response to viscosity setpoint changes, PI controller with  $k_c = .4$  and  $\tau_i = 40$  s.

output had a large variance about the setpoint; the controller was found to be too sensitive to noise in the viscosity signal. It was then detuned slightly, and the resulting system response to setpoint changes for  $k_c = .4$  and  $\tau_1 = 40$  s is displayed in Figure 8-3. The controller tended to ring at high viscosity, where the standard deviation about the setpoint was over 11 Pa s, as compared with less than 9 Pa s at lower viscosities. The response was slower at low viscosity; rise times, especially for down steps, were 60 s longer than at high viscosity.

This difference in the speed of the response was expected. The reduced process gain at low viscosity caused the controller, which was tuned to perform with a more quickly reacting system, to become sluggish at low viscosity. Also, with large viscosity steps, viscous flushing context cause steps upward to respond more quickly than steps downward. Both of these nonlinearities were addressed to improve the process response.

# 8.2 PI Controller with Gain Scheduling

Two nonlinearities had to be addressed to improve the controller response. The first was the varying process gain,  $k_p$ , which is an approximately linear function of viscosity (see Figure 7-7). When modelling a first order process with a PI controller, the speed of the response is controlled largely by the product  $k_pk_c$ . Gain scheduling is achieved by forcing  $k_pk_c$  to be constant. After measuring the viscosity, a value of  $k_p$  is calculated using the function determined in section 7.2.1. The constant  $k_pk_c$  is then used to compute a  $k_c$  that will give the desired speed of response.

When implementing the gain scheduling,  $k_c$  becomes a variable, changing with time. The control equation must change slightly from (8-5) to reflect this:

$$\Delta u_t = (k_C)_t \left(1 + \frac{\Delta t_C}{\tau_I}\right) e_t - (k_C)_{t-1} e_{t-1}$$
(8-6)

with  $(k_c)_t$  now a function of time.

The second nonlinearity was the flushing effect. A "gain factor" was used to either raise or lower the magnitude of the first control action after a setpoint change by multiplying  $k_c$  by a factor. The process reacted faster to an increase in the setpoint, so the factor,  $G_{KU}$  was less than one for the up step to reduce the size of the initial response. A factor,  $G_{KD}$  greater than one was used to boost the more sluggish down step. This tended to even out the up/down step nonlinearity, so that the controller could be tuned to higher gains without the up step response becoming oscillatory.

# 8.2.1 Setpoint Tracking

In order to establish a reasonable value for  $k_pk_c$ , the control experiments of section 8.1 were examined to find ranges where the PI controller was performing well. Figure 8-3 shows that the controller worked well at the medium viscosity level. Using the linear relationship from Figure 7-7 at  $\eta$ =800 Pa·s we find  $k_p$ =-0.77. Since  $k_c$  is 0.4 for that experiment,  $k_pk_c$  is 0.31. The gain factors for the flushing effect correction were determined empirically to be  $G_{KU}$ =0.85 for the up step and  $G_{KD}$ =1.1 for the down step.





In Figure 8-4, it can be seen that the response was slower than in Figure 8-3 in the high viscosity range, with an overshoot but no ringing. The low viscosity range responded much more quickly than before. While the response was no longer a function of viscosity due to the gain scheduling, the up steps still reacted somewhat faster than the down steps. Incorporating the "flushing effect" factors did not completely remove this nonlinearity, since it operated only on the first control action after a setpoint change.

The down step responses were critically damped, with a rise time of 105 s. The up steps had a rise time of 75 s with a slight oscillation, taking an extra 100 s to completely settle down. The controlled variable, peroxide concentration, generally stabilized after two control periods for both up and down steps.



Figure 8-5 Response of process to large and small amplitude setpoint changes, PI controller with gain scheduling and flushing effect gain factors,  $k_pk_c=.31$ ,  $\tau_I=40$  s

Figure 8-5 shows several large and small steps. The three small steps show no flushing effects and were critically damped with a rise time of 120 s. The large steps, however, were dominated by this effect. The down step had a very long response time of 270 s because a very low viscosity polymer was trying to purge a relatively high viscosity polymer from the system; changing the gain for one period was not enough to completely compensate for this effect. The large up step shows a more pronounced oscillation, with a rise time of 75 s but a final settling time of about 300 s. The large up and down steps had similar settling times but different shapes due to the flushing nonlinearity.

# 8.2.2 Disturbance Rejection

Disturbances were generated by changing the value of MBCN, the variable in the control program that reflected the concentration of the peroxide masterbatch. The bottom graph of Figure 8-6 shows the actual and demanded amounts of peroxide fed to the extruder. Changing the value of MBCN during an experiment caused the computer to request the wrong amount of masterbatch and simulated a step change in the masterbatch concentration.



Figure 8-6 Disturbance rejection of PI controller with gain scheduling,  $k_pk_c = .31$ ,  $\tau_I = 40$  s,  $\eta_{seept} = 800$  Pa/s. The actual masterbatch concentration is 1000 ppm.

Figure 8-6 shows the process operating at about 250 ppm peroxide to maintain an 800 Pass setpoint. After each disturbance (when the value of MBCN was changed), the actual concentration quickly returned to the 250 ppm region. MBCN, which was set

initially to 1000 ppm, was altered up and down by 25%. In each of the four disturbances, the process recovered after 3 control periods, or about 225 s.

Other disturbances, such as mixing handfuls of raw polypropylene with the masterbatch, did not result in any appreciable fluctuation in the process viscosity. These disturbances caused slow drifts, to which the controller responded. Any change in viscosity was small enough to be very difficult to pick out of the process noise. Filtering the viscosity measurement may have improved the resolution somewhat, but would have slowed the process response. It was decided to use filtering only with the minimum variance controller, which has a process noise filter built into it.

# 8.3 A Minimum Variance Controller with Gain Scheduling

Minimum variance controllers (MVC) are model based and include dead time compensation, thus performing better than PID controllers for systems with significant dead time. The Smith Predictor and Dahlin algorithms, as noted in section 8.3.2, are special cases of the MVC, each optimized for a particular type of process disturbance. The MVC methodology is more versatile because its formulation is more general and allows the structure of a controller to be optimized to reject disturbances specific to a process (i.e. steps, long term drift, and/or oscillations). The MVC, for systems with an invertible process model, is an optimal controller for noisy processes. (Note that there are other, more complex MVC design procedures which can handle non-invertible models [50]).

Rather than using an error function for its performance criterion (i.e. IAE for the PI controller, section 8.1.1), the MVC is designed to minimize the variance of the deviations of the process output from the setpoint [51]. The controller is composed of three elements. The predictor, based on the process noise model, forecasts the effect of future disturbances on the process output. The control action component uses the inverted process dynamics model to calculate the control signal necessary to set the predicted value equal to the setpoint value. The dead time compensator provides filtering

and allows for previous control actions that have not yet worked their way through the process.

## 8.3.1 Developing the Minimum Variance Controller

The full process model developed in chapter 7 incorporates both the dynamic and noise models, (7-2) and (7-4):

$$\eta_t = \frac{(\omega_0 + \omega_1 z^{-1}) z^{-3}}{1 - \delta z^{-1}} u_t + \frac{1 - \theta z^{-1}}{1 - z^{-1}} a_t$$
(8-7)

where  $\eta_t$  and  $u_t$  are the deviation viscosity and peroxide concentration at time t  $\omega_0, \omega_1, \delta$  and  $\theta$  are the model parameters  $a_t$  is a white noise signal

 $z^{-1}$  is the backwards shift operator

Note that the deviation variables are defined as  $V_t = V_{abs} - V_{scept}$ , the negative of the values used for the PI controller. A control period of 25 s was chosen, giving an invertible model suitable for use in the controller. This gave two entire periods of dead time (f=2), and led to the  $z^3$  term in the model (three lag periods, two of dead time, one of zero order hold). Macgregor [51] recommends not more than three periods of dead time for stability reasons.

The controller uses the process model to offset any disturbances to the process. It is desired to keep  $\eta_t=0$  (no deviation). From (8-7),

This is obviously physically impossible, since it requires future values of the disturbances. Instead, a minimum variance forecast of the process noise is used to predict future values, and the control action  $u_t$  is estimated from these. The three-step-ahead value of the noise can be expressed as (see Appendix A)

$$N_{t+3} = \left(1 + (1-\theta)z^{-1} + (1-\theta)z^{-2}\right)a_{t+3} + \frac{(1-\theta)z^{-3}}{1-z^{-1}}a_t$$
(8-9)

The second term is the transfer function of the minimum mean square error (MMSE) disturbance predictor, using only information known at time t. The first term is the error in the forecast, made up of future shocks (or disturbances) to the system.

Looking at (8-9), it can be seen that as the process becomes noisier and  $\theta$  becomes large, (1- $\theta$ ) becomes small, and the predictor estimates small, conservative changes. The controller will react slowly to any significant fluctuations in the process. Decreasing  $\theta$  will cause more aggressive forecasting and a faster response; in a noisy system, however, this can lead to an unstable controller.

The number of periods of dead time also have a large effect on the accuracy of a prediction. Every additional period of dead time adds another term to the error in the forecast, reducing the effectiveness of the controller. Even though the MVC methodology includes dead time compensation, every effort should be made to keep the dead time as short as possible during process design.

The full controller, derived in Appendix A, is as follows:

المنعبة الم

$$u_{t} = \frac{1-\theta}{1-z^{-1}} \cdot \frac{1-\delta z^{-1}}{\omega_{0}+\omega_{1}z^{-1}} \cdot \frac{1}{1+(1-\theta)z^{-1}+(1-\theta)z^{-2}} \cdot \eta_{t}$$
 (8-10)

The first term is the transfer function of the predictor, the second term is the inverted process dynamics model, and the final term provides dead time compensation. Integral action is supplied by the  $1-z^1$  term in the denominator of the predictor, since

$$(1-z^{-1})^{-1} = 1+z^{-1}+z^{-2}+\dots$$
 (8-11)

provides a summing action. Mathematically, the form of the controller is identical to that of a Dahlin controller [51]. The noise model parameter  $\theta$  is equivalent to  $\lambda$ , the closed loop time constant from the Dahlin controller.

The actual control equation used was the velocity form of (8-10). When the backward-shift operators are expanded (i.e.  $z^{-1} \cdot u_t = u_{t-1}$ ) and terms are collected, the velocity form is

$$\Delta u_{t} = \frac{(\omega_{1} - a\omega_{0})\Delta u_{t-1} + (a\omega_{1} - a\omega_{0})\Delta u_{t-2} + a\omega_{1}\Delta u_{t-3} + a(\eta_{t} - \delta\eta_{t-1})}{\omega_{0}}$$
(8-12)

where  $a=(1-\theta)$ . The current and previous viscosity readings, and the last four control actions (or last three differences) were needed to calculate the current control action.

The gain scheduling was implemented by making  $\omega_0$  and  $\omega_1$  functions of viscosity, in much the same manner as was done for the PI controller. Reference gain parameters

Table 8-2 Values of the gain parameters at various viscosity levels. The fractions of the reference gains, G, used to determine the linear gain function are also displayed.

η (Pa·s)	ω	ω <sub>1</sub>	G
892	430	250	1
782	354	205	.822
655	190	155	.622

were multiplied by a linear factor, G, that reduced the gain of the process model as the viscosity decreased. Table 8-2 shows the gain parameters determined from PRBS experiments with  $\Delta t=25$  s at high, medium and low viscosity. At high viscosity, G was arbitrarily set to one, making the gain parameters  $\omega_0$  and  $\omega_1$  for that experiment the reference values. The other values of G are the fraction that the gain was reduced. A linear regression was employed to fit G as a function of viscosity

$$G = \frac{\eta}{627} - .423$$
 (8-13)

As expected, (8-13) has approximately the same slope as the function calculated in Figure 7-7 for the continuous time model parameter  $k_p$ . Values of  $\omega$  for the controller were calculated by multiplying the reference gain values by  $G(\eta)$ . Only the  $\omega_0$  parameter at low viscosity was not fitted well by (8-13); that reference gain fraction was lower than the linear model predicted. This resulted in a slightly high estimate of  $\omega_0$  at low viscosity, erring on the side of conservatism and giving the controller a slower response in this region.

Since the process gain now varies with time, care must be taken to use the correct gain parameters with the correct control action to get the proper dead time compensation. (8-12) can be modified slightly to give:

$$\Delta u_{t} = \frac{\left[(\omega_{1} - a\omega_{0})\Delta u\right]_{t-1} + \left[(a\omega_{1} - a\omega_{0})\Delta u\right]_{t-2} + \left[a\omega_{1}\Delta u\right]_{t-3} + a(\eta_{t} - \delta\eta_{t-1})}{\left[\omega_{0}\right]_{t}}$$
(8-14)

## 8.3.2 Setpoint Tracking

Once the gain function was determined, the only adjustable parameter left in the controller was  $\theta$ , which controlled the amount of filtering the controller performed and thus the speed of its response. Identification experiments (section 7.2.2) suggested that a value of  $\theta = 0.65$  should be employed.

Figure 8-7 shows the response of the closed loop process to a number of changes in setpoint. The average response has about 200 s rise time for both up and down steps. The response is critically damped, with the setpoint changes not large enough for the flushing effect to influence the results. There was an outlying measurement at about 2300 s, just as the setpoint was changed. While it can be seen that the controlled variable oscillated for several periods after the disturbance, the process recovered very quickly and there was very little oscillation in the viscosity. The controller is quite stable.

The effect of changing bags of polypropylene can be seen here as well; just after 1500 s, the viscosity begins to drift upwards as the new polymer begins to feed through. The concentration of peroxide increases from just over 300 ppm to almost 350 ppm to offset this disturbance. Looking at the start and finish of the run, where  $\eta_{sept}$ =925 Pa·s,





the process has shifted from about 200 ppm to almost 250 ppm peroxide. An increase in the stabilizer concentration from the first bag of polypropylene to the second is the most likely source of this disturbance, requiring extra peroxide to react. This adds an offset to  $u_t$ , but does not change the process gain.

Various values of  $\theta$  were examined to see what effect changing this parameter would have on the performance of the controller. Figure 8-8 shows setpoint tracking



with  $\theta = 0.55$ , using steps similar to those used to test the PI controllers. The first viscosity down step had a rise time of 190 s while the second step had a rise time of 220 s. The difference occurred because the gain scheduling employed higher than actual gains at low viscosity, slowing the controller's response in that region. The response on the down step was slower than that of the PI controller shown in Figure 8-4 because there is no boost on the initial step after the setpoint change. The response to an up step in viscosity setpoint, with rise times of 75 s, was considerably faster than the PI controller, again because no correction for the flushing effect was made. The MVC, with  $\Delta t_c = 25$ 



Figure 8-9 Response of the gain scheduled MVC to setpoint changes,  $\theta = 0.75$ .

s, performed control actions three times more often than the PI controllers and could respond fast enough to the quick upsurge in viscosity that no overshoot or oscillations occurred.

Figure 8-9 shows the same setpoint changes as Figure 8-8, except that  $\theta = 0.75$ . As was expected, the response time to the changes was longer; 230 and 260 s for the down steps and 170 and 115 s for the up steps. Again, setpoint changes at a higher viscosity had faster response times, and the flushing effect was still in evidence. It can be seen in the lower graphs, showing the controlled variable (peroxide concentration), that the controller with  $\theta = 0.55$  approached its new level much more aggressively than with  $\theta = 0.75$ . The standard deviations of the viscosity at steady state for the controllers in this section and the PI controllers in section 8.2 are approximately the same, and are at the same level as those achieved during open loop measurements (around  $\pm 7$  Pa-s at high viscosity, to  $\pm 11$  Pa-s at low viscosity). This implies that the noise in the viscosity readings was from the rheometer, and that the process viscosity was as constant as could be determined given the signal to noise ratio.

#### 8.3.3 Disturbance Rejection

The first series of disturbances were similar to those used to test the PI controllers. They were not exactly the same because an equipment failure did not allow the full series of disturbance tests to be run. The variable MBCN in the control program was changed to simulate a step change in masterbatch concentration. Figure 8-10 shows a typical result. The steps used were not as large as those in Figure 8-6, but the middle step, from MBCN=900 to 1100 ppm did give a fair peak at about 900 s. The system takes 200 s to recover from this disturbance. The other steps, with magnitudes of only 100 ppm, caused enough drift to allow the response of the system to be seen, but the details were blurred by process noise. They appeared to have recovery times of about the same order of magnitude as the 200 ppm step (about 200 s), as did repeats of this experiment at other viscosity setpoint levels. This was slightly faster than the PI controller response, because the MVC sampled more often and could therefore respond more quickly to a disturbance.

A slightly different disturbance was used to examine the effect of  $\theta$  on the recovery time. The actual masterbatch in the feeder was switched from 1000 ppm to 500 ppm (or vice versa) to see how the controller would handle a real rather than simulated change in masterbatch concentration. When the feeder was almost empty (approximately 200 g remaining), the new masterbatch was added. This was not as sharp a step disturbance and was not as reproducible. The feeder tended to mix the two masterbatch concentrations somewhat while feeding to the extruder, blurring the step change and increasing the response time. Experiments to examine the open loop response to this disturbance showed a large variation in  $\tau_{\rm p}$ , between 50 and 70 s. These were higher than



Figure 8-10 Response of the gain scheduled MVC to simulated step disturbances in masterbatch concentration.

the time constants obtained in open loop identification runs for computer controlled step changes.

Figure 8-11 shows a typical example of the response to a switch from masterbatch A (1000 ppm) to masterbatch B (500 ppm) and back again. Due to the nature of the disturbance, it was difficult to specify exactly when it entered the system. The feeder had to finish feeding the old material before the new could start. The response was measured from the time when the controller began to react. In Figure 8-11, the process recovers from the switch to 500 ppm in 290 s, and from the switch back to 1000 ppm in 250 s. The same experiment with  $\theta$ =0.8 took about 400 s to recover. While the disturbance is not as repeatable as the simulated concentration steps, reasonable results



Figure 8-11 Response of the gain scheduled MVC to changing masterbatch concentrations, from 1000 to 500 ppm and back again. MBCN=1000 ppm,  $\theta$ =0.6. were obtained. Only one experiment produced a result more than 10% from the mean

response time for any given set of repeats.

Large changes in the masterbatch concentration could have an effect on the stability of the MVC. As the concentration moved away from the nominal value used in the control program (variable MBCN), the effective gain of the controller changed. If MBCN=1000 ppm, as in Figure 8-11, and the actual concentration was only 500 ppm, then any change in the concentration setpoint,  $\Delta u$ , was only half as effective as it should be, making the controller sluggish. If MBCN=500 ppm while the actual concentration was 1000 ppm, the controller had twice the effect with any control action, which could lead to instability. In Figure 8-12 the controller response to the disturbance, with  $\theta$ =0.8



Figure 8-12 Response of gain scheduled MVC to changing masterbatch concentration, 500 to 1000 to 500 ppm. MBCN=500 ppm,  $\theta$ =0.8.

but twice the effective controller gain, was faster than in Figure 8-11 where there was only half the normal gain. The switch to 1000 ppm masterbatch took about 225 s, while the switch back to 500 ppm took about 290 s. There appeared to be some oscillation, however, so the final settling times were longer.

While concentration drift was not a problem for small changes in masterbatch concentration, controller performance could deteriorate considerably for large drifts, which may occur very slowly. Self-tuning regulators are designed to handle this kind of problem, but are beyond the scope of this thesis.

Both the nonlinear process gain and the flushing effect are evident in the disturbance rejection experiments. Disturbances causing elevations in the viscosity are

of greater magnitude than downwards shocks, since the process gain is higher at high viscosity. Also, down shifts recover more quickly than up shifts as high viscosity materials purge lower more quickly than vice-versa.

## 8.4 Summary of Control Experiment Results

The PI controller was hampered in its response to disturbances by long control periods and a lack of filtering of process noise. Gain scheduling was used to improve the performance of the controller in the low viscosity region, where the process gain was smaller by a factor of almost one half. The effect of a second nonlinearity in the system, called the flushing effect, was reduced for setpoint changes through the use of flushing factors. This factor reduced the control action for an up step in setpoint, and boosted the controller response to a down step.

The MVC was able to act three times more often than the PI controller due to its dead time compensation. Gain scheduling was implemented to better the low viscosity performance, but the flushing effect factors were not used; the controller sampled quickly enough that it adjusted itself to the nonlinear process response. The noise model parameter,  $\theta$ , was used to control the sensitivity of the controller to process fluctuations. It was found that a value of  $\theta = .55$  provided a fast, stable response.

The two controllers had comparable performances. Due to its initial step gain factor algorithm, the PI controller was faster for small setpoint changes (about 120 s verses 200 s rise times). The MVC was faster for large changes (300 s for the PI controller verses 200 s for an up step and 75 s for a down step for the MVC) because its higher sampling rate allowed it to better adapt to process nonlinearities. Disturbance rejection was similar for the two controllers, with the MVC being slightly faster (200 s verses about 225 s for the PI controller).

One of the advantages of using the MVC is that it can be made self-tuning. Gain scheduling can be used to get first estimates of model parameters when the process moves to a different range of viscosity; the self-tuning algorithm could then fine tune for optimum performance. Even the fractional period of dead time in the process model

could be adjusted, by varying the ratio of the two gain parameters  $\omega_0$  and  $\omega_1$ . The values of the parameters can be compared with historical values to monitor for process equipment failure.

-

.

# CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS

This chapter contains the overall conclusions and recommendations yielded by this project. The capabilities of the in-line rheometer (ILR) and its application as a control sensor are discussed, as well as the results garnered from control experiments performed with the polypropylene visbreaking process. Contributions to knowledge are listed, and some suggestions for future work are provided.

# 9.1 Conclusions

# 9.1.1 The Suitability of the ILR as a Process Rheometer

In general the ILR performed quite well as a viscometer, particularly at higher shear rates (about 30 1/s); the shear stresses due to the rotating drum were high relative to noise in the system. Viscosity curves measured by the ILR were found to be in good agreement with results from other rheometers, with an average discrepancy of 4% and a maximum deviation of 10%. The major sources of error in the ILR are the effects of pressure on the SST and the temperature uncertainty in the measurement gap. Techniques were developed to compensate for both the contributions of pressure flow when measuring the stress in the shearing gap and the effects of the pressure on the SST baseline, reducing the variance in the readings. Due to the flow rates of material through the instrument, direct control of the melt temperature in the measuring gap is difficult if not impossible. The rheometer was run 9°C higher than the extruder to allow for shear heating of the polymer; the polymer in the measurement gap was determined (through indirect measurements and calculations) to be within  $\pm 2°C$  of this value.

Dynamic mechanical analysis (DMA) was attempted with the ILR. Frequency transform techniques were developed to obtain results over a wide frequency range with a single waveform. FFT analysis of a pseudo-random binary sequence strain waveform was used to obtain a G'-G" curve over two decades of frequency. This method worked

well in the lab but, when DMA was attempted with the ILR, problems arose. The design of the SST allowed polymer into the lower cavity of the SST housing through the gap around the face of the active beam. The polymer damped the response of the SST, reducing its frequency response below that necessary for the DMA measurements. The resulting distortion of the phase of the complex modulus  $G^*$  rendered the measurements inaccurate.

Residence time studies of the extruder and rheometer, along with the dynamic process information discussed in the next section, were used to estimate the dynamic response of the rheometer to changes in the rheology of the process flow. Techniques were developed and incorporated into the measurement cycle to aid in the sample renewal in the measurement zone, as well as to reduce polymer recirculation zones in the rheometer cavity. With a material flow rate of 12 kg/hr, the ILR demonstrated a dead time of 6 s (from the time the material reached the entrance of the rheometer) and a first order time constant of less than 15 s. The ILR exhibited a faster response than any available commercial rheometer due to its in-line design. This made it ideal for viscosity control applications.

# 9.1.2 Control of the Polypropylene Visbreaking Process

The ILR was used to control the viscosity of a polypropylene visbreaking process. Stochastic identification methods were used to determine the dynamic response of the system, which was modelled as a first order plus dead time process. The process (including the rheometer) had a time constant of about 15 s, with a dead time of slightly less than a minute. Feedback control, established using proportional-integral (PI) and minimum variance controllers (MVC), was effective for both setpoint tracking and disturbance rejection. Gain scheduling was incorporated into both controllers to cope with a non-constant process gain, which varied with viscosity levels. The PI controller was detuned to allow for the dead time in the response, and further modified with gain factors to account for non-linearities in the time constant. These modifications were not

necessary for the MVC, which could take control actions more often (every 25 s as opposed to every 75 s for the PI controller) due to its dead time compensation.

The two controllers gave about the same performance for setpoint tracking, with about a 200 s rise time to a new viscosity setpoint with little or no oscillation. The MVC rejected disturbances faster than the PI controller due to its faster sampling, recovering in about 200 s where the PI controller required 225 s. Another advantage to the MVC is that it is easier to adjust the sensitivity of the controller response; the single parameter  $\theta$  is used to control the amount of filtering performed by the controller, and hence the speed of its response to process changes. The tuning of a PI controller is more complex, since the two tuning parameters are inter-dependent.

Overall, control of the process was excellent. The response times of the process to setpoint changes and disturbances is considerably faster than found in any previous study, due largely to the faster response of the ILR. The MVC is the controller of choice. While some extra work is required to determine a process model, this is more than made up for by dead time compensation, process noise filtering and ease of adjustment.

#### 9.2 Contributions to Knowledge

1) This project has advanced the technology of process rheometry. In particular, an in-line rheometer was designed incorporating the concept of the SST, which had been successfully used in the laboratory sliding plate rheometer. The effect of pressure and pressure generated flows on the SST signal was determined with the SST, and an algorithm to use this information to correct viscosity readings was implemented. Measurement techniques to improve sample renewal in the measurement zone and minimize the rheometer response time were developed. Viscosity results from the ILR compare well with other lab instruments for polypropylene, and the feasibility of the ILR as a control sensor was demonstrated.

2) Techniques were developed to perform dynamic mechanical analysis measurements over a range of frequencies with a single complex waveform, using Fourier transforms to analyze the data. Storage and loss moduli curves over a two decade range of frequency were determined in a period slightly longer than the period of the lowest measured frequency component. This greatly reduces the amount of time required to obtain a curve compared with the multiple-sinusoid single-point method.

3) The dynamics of the polypropylene visbreaking process were studied using the ILR. The ILR gave a much truer tracking of the process' dynamic response due to its faster response. The study indicated that the process was readily controllable, especially with controllers incorporating dead time compensation. Non-linearities in the process gain and the first order time constant were identified. Gain scheduling was implemented in both the MVC and PI controllers to compensate for a non-constant process gain, and a gain factor was used with the PI controller to compensate for the non-linear first order time constant.

#### 9.3 Recommendations and Suggestions for Future Study

It is recommended that the rheometer pressure transducers be placed closer to or just inside the shearing gap to get a more accurate measurement of the pressure drop across the measurement zone. Also, a reliable means of directly determining the melt temperature in the gap will improve the accuracy of the rheometer. Determining melt temperatures in a one mm slit is difficult, since sensors usually report the metal temperature. A non-intrusive probe, such as an infra-red type, may provide satisfactory data. Better temperature control of the rheometer, particularly of the shearing drum, would also reduce temperature effects.

Future SST designs need to address a number of items. The active face of the SST must be sealed in order to avoid the entrance of process material into the housing, and this must be performed in such a way as to avoid damping the frequency response. This will be a challenge, given the operating temperatures of this process (over 200°C). Ideally, for general use with a range of common polymers, an industrial version of the

SST would be expected to withstand temperatures of at least 350°C. Better control of the housing temperature is also required, or a change in design to reduce the sensitivity of the SST baseline signal to the housing temperature. The mounting and adjustment of the capacitance probe requires considerable effort and could be redesigned to ease use. Also, the effect of pressure on the SST must be addressed, since large scale polymer production lines often run at pressures of 20 MPa or higher. This study was performed with process pressures of less than 3 MPa.

The work started here involving DMA using complex waveforms is very promising. The arbitrary strain generation system on the rheometer functioned well; only the dynamic response of the SST needed improvement. A related area that would require some study before implementing the in-line DMA measurements is the effect of a pressure flow superposed on the DMA measurement.

There are a number of interesting areas to be explored as far as controlling the visbreaking process is concerned. The first is to use a self-tuning, or adaptive, minimum variance controller. This controller monitors and adjusts the fit of its process model, optimizing itself around the control setpoint. This eliminates the need for gain scheduling, since the controller determines the appropriate gain setting automatically.

Another area of interest is closer control of the molecular weight distribution (MWD) of the polypropylene. Two variables are used to characterize the MWD, the weight-average molecular weight,  $M_w$ , and polydispersity,  $M_w/M_n$ . Ideally, both of these parameters should be controlled, but since the only manipulated variable is peroxide concentration, generally only  $M_w$  is measured and controlled (low-shear-rate viscosity correlates with  $M_w$ ). In a twin screw extruder, a second manipulated variable to consider is the screw speed, which determines the amount of mixing between the raw polypropylene and the peroxide coated masterbatch. Poorer mixing of the peroxide (slower screw speeds) could lead to uneven degradation in the melt, broadening the MWD. Careful control of the barrel temperatures and screw configuration can also be used to control the temperature of the melt, and thus the speed of the reaction of the peroxide, which will determine how much mixing occurs before the degradation reaction

is complete. Further study in this area could determine if this is a feasible method of influencing  $M_w/M_n$  independently of  $M_w$ .

.

#### **REFERENCES**

- Dealy, J. M., "Method of Measuring Shear Stress", U. S. Patent 4 463 928, 1984.
- 2 Dealy, J. M., " Method and Apparatus for Measuring Rheological Properties of Fluids", U. S. Patent 4 571 989, 1986.
- 3. Giacomin, A. J., <u>A Sliding Plate Melt Rheometer Incorporating a Shear Stress</u> <u>Transducer</u>, Ph. D. Thesis, McGill University, Montreal, Canada, 1987.
- Giacomin, A. J. and Dealy, J. M., " A New Rheometer for Molten Plastics", SPE Tech. Papers, <u>32</u>, 711, 1987.
- 5. Yazak, G. and Diraddo, R. W., "An Inside Look at Extrusion Melt Temperatures", Plastics Tech., June, 61, 1993.
- 6. Goettfert, 488 Lakeshore Parkway, Rock Hill, SC 29730
- Seiscor Instruments, now a division of Kayeness, P.O. Box 709, Morgantown PA 19543
- Goettfert, A., "New Concept for On-line Rheometry in Real Time", Kunststoffe, <u>81</u>, 21, 1991.
- 9. Rheometrics, Inc., Piscataway, N.J.
- 10. Fritz, H-G and Stoehrer, B., "Polymer Compounding Process for Controlled Peroxide Degradation of PP", Intern. Polymer Processing 1, 31, 1986.

- Pabedinskas, A., Cluett, W. R., and Balke, S. T., "Development of an In-line Rheometer Suitable for Reactive Extrusion Processes", Polym. Eng. Sci., <u>31</u> (5), 365, 1991.
- 12. Broadhead, T. O., <u>Development of an In-line Rheometer for Control of Reactive</u> <u>Extrusion</u>, Ph. D. Thesis, McGill University, Montreal, Canada, 1992.
- 13. Dragan, S. P., <u>Motion Generation and Data Acquisition for a Rotational Process</u> <u>Rheometer</u>, M. Eng Thesis, McGill University, Montreal, Canada, 1989.
- 14. Bubic, F. R., "Kinematics and Dynamics of No: 3.45 Rheometer Oscillatroy Drive: Design Notes", McGill University, Montreal, Canada, 1989.
- 15. Natta, G., "Kinetic Studies of  $\alpha$ -Olefin Polymerization", J. Poly. Sci., <u>34</u>, 21, 1959.
- Tzoganakis, C., Vlachopoulos, J., and Hamielec, A. E., "Production of CR-PP Resins by Peroxide Promoted Degradation During Extrusion", Poly. Eng. Sci., <u>28</u>, 170, 1988.
- 17. Tzoganakis, C., Vlachopoulos, J., and Hamielec, A. E., "Controlled Degradation of Polypropylene", Chem. Eng. Process, November, <u>84</u>, 47, 1988.
- Tzoganakis, C., Vlachopoulos, J., and Hamielec, A. E., "Effect of Molecular Weight Distribution on the Rheological and Mechanical Properties of Polypropylene", Poly. Eng. Sci., <u>29</u> (6), 390, 1989.
- Suwanda, D., Lew, R., and Balke, S. T., "The Reactive Extrusion of Polypropylene", 36th Canadian Chemical Engineering Conference, Sarnia, Ontario, Canada, 1986.

14

- 20. Curry, J., Werner & Pfleiderer Corp., Ramsey, New Jersey, "Private Communications", March 1989.
- 21. Balke, S. T., Suwanda, D. and Lew, R., " A Kinetic Model for the Degradation of Polypropylene", J. Poly. Sci., Part C: Polymer Letters, <u>25</u>, 313, 1987.
- 22. Tzoganakis, C., Vlachopoulos, J., and Hamielec, A. E., "Modelling of the Peroxide Degradation of PP", Intern. Polymer Processing III, 3, 1988.
- 23. "Reactions and Polymerizations Using Co-rotating Intermeshing Twin-Screw Extruders", Werner & Pfleiderer Corp., Ramsey, New Jersey.
- 24. Zeichner, G. R. and Patel, P. D., " A Comprehensive Evaluation of PP Melt Rheology", 53<sup>rd</sup> Annual Meeting, Soc. of Rheology, Louisville, Ky, Oct., 1981.
- Curry, J. and Jackson, S., "Free Radical Degradation of Polypropylene", Chem. Eng. Process, December, 43, 1988.

4

- 26. Pabedinskas, A., Cluett, W. R. and Balke, S. T., "Process Control for PP Degradation During Reaction Extrusion", Polym. Eng. Sci., 29, 993, 1989.
- Dumoulin, M. M., Daigneault, L. E., Gendron, R. and Dufour, J., "On-line Rheology Control for the Peroxide Degradation of PP", ANTEC 1993 Conference Proceedings, New York, 1993.
- 28. Balke, S. T., Private Communicaton, University of Toronto, Toronto, Canada, 1989.

- Curry, J., Kiani, A. and Dreiblatt, A., "Feed Variance Limitations for Co-Rotating Intermeshing Twin Screw Extruders", Technical Report, Werner & Pfleiderer Corp., Ramsey, New Jersey, 1991.
- 30. Tuminello, W. H., Polymer Engineering Science, <u>26</u>, 1339, 1986.
- Holly, E. K., Venkataraman, S. K., Chambon, F. and Winter, H. H., "Fourier Transform Mechanical Spectroscopy of Viscoelastic Materials with Transient Structure", J. Non-Newton. Fluid. Mech., <u>26</u>, 10, 1987.
- 32. Cooley, J. W. and Tukey, J. W., "", Mathematical Computing, <u>19</u>, 297, 1965.
- Ramirez, R. W., "The FFT- Fundamentals and Concepts", Prentice Hall, Englewood Cliffs, N. J., 1985.
- Marin, G., Peyrelasse, J. and Monge, Ph., "A New Method for Evaluating the Dynamic Properties of Polymers: Time Domain Mechanical Spectroscopy", Rheologica Acta, <u>22</u>, 476, 1983.
- Malkin, A. Ya., Beghishev, V. P. and Mansurov, V. A., "A Method of Non-Harmonic Vibration for Determining Mechanical Properties for Polymeric Materials", Vysokomol. Soedin. (J. Polymer Sci USSR), <u>26A</u>, N4, 869, 1984.
- Bertig, J. P., O'Connor, J. J. and Grehlinger, M., "Use of Arbitrary Waveforms to Determine the Rheological Properties of Viscoelastic Systems", Society of Rheology, 61st Annual Meeting, Montreal, Canada, 1989.
- Nelson, B. I. and Dealy, J. M., "Dynamic Mechanical Analysis Using Complex Waveforms", Chapter 7, <u>Techniques in Rheological Measurement</u>, Collyer and Clegg, Editors, Chapman and Hall, London, 1993.
- Davies, W. D. T., <u>System Identification for Self-Adaptive Control</u>, Wiley Inter-Science, New York, 1970.
- Vratsanos, M. S. and Farris, R. J., "A Method for Calculating Dynamic Mechanical Properties Using Fourier Transforms of Pulse Deformation Experiments", J. Appl. Polym. Sci., <u>36</u>, 403, 1988.
- 40. Nelson, B. I., <u>An Improved In-line Process Rheometer for Use as a Process</u> <u>Control Sensor</u>, M. Eng Thesis, McGill University, Montreal, Canada, 1988.
- 41. Hatzikiriakos, S., Ph. D. Thesis, McGill University, Montreal, Canada, 1992.
- 42. Tadmor, Z. and Gogos, C., <u>Principles of Polymer Processing</u>, John Wiley and Sons, New York, 1979.
- 43. Schummer, P. and Worthoff, R. H., Chem. Eng. Sci., <u>33</u>, 759, 1978.
- Flumerfelt, R. W., Pierick, M. W., Cooper, S. L., and Bird, R. B., I & EC Fundamentals, <u>8</u> (2), 354, 1969.
- 45. Curry, J. and Jackson, S. "Control Strategy for Free Radical Degradation of Polypropylene Via REX", AIChE Annual Meeting, New York, 1987.
- 46. Isermann, R., Digital Control Systems, Springer-Verlag, New York, 1981.
- 47. Palmor, Z. J. and Shinnar, R., I & E C Proc. Des. Dev., <u>18</u> (1), 8, 1979.
- 48. Chen, T., <u>An On-Line Residence Time Distribution Measurement in a ZSK Twin</u> <u>Screw Exruder</u>, M.Eng. Thesis, McGill University, Montreal, Canada, 1992.

- 49. Stephanopoulos, G., <u>Chemical Process Control: An Introduction to Theory and</u> <u>Practice</u>, Prentice Hall, Englewood Cliffs, NJ, 1984.
- 50. Astrom, K.J. and Wittenmark, B., <u>Computer Controlled Systems: Theory and</u> <u>Design</u>, Second Edition, Prentice Hall, Englewood Cliffs, NJ, 1990.
- MacGregor, J. F., <u>Optimal Stochastic Control Theory and Applications</u>, Course notes, Dept of Chemical Engineering, McMaster University, Hamilton, Canada, 1989.
- 52. Box, G. E. P. and Jenkins, G. M., <u>Time Series Analysis: Forecasting and</u> <u>Control (Revised Edition)</u>, Holden-Day, Inc., San Francisco, California, 1976.

# **APPENDIX A**

# DERIVATION OF THE MVC EQUATION, SAMPLE PROCESS IDENTIFICATION CALCULATION

#### APPENDIX A

### A.1 Derivation of the Minimum Variance Controller

All process controllers are designed to optimize some form of performance criterion. PID controllers are tuned to compromise between two objectives, the speed of the controller response and the permissable overshoot and resulting process oscillations. The performance criterion for minimum variance controllers (MVC) is to minimize the variance of the output deviation around the process setpoint. The MVC uses discrete process and noise models of the system to be controlled to achieve this.

The general form of the discrete process model is

$$Y_{t} = \frac{\omega(z^{-1})}{\delta(z^{-1})} U_{t-f-1} + N_{t}$$
 (A-1)

where  $Y_t = y_t - y_{setpt}$  is the process output in deviation form  $U_t = u_t - u_{setpt}$  is the process input in deviation form  $\omega(z^{-1}) =$ moving average part of model (process gains)  $\delta(z^{-1}) =$ auto-regressive part of model (time constants)

f = the number of whole periods of dead time

and the noise model is

$$N_t = \frac{\theta(z^{-1})}{\phi(z^{-1})} a_t \tag{A-2}$$

where  $N_t = process$  disturbance at time t

 $a_t$  = white noise signal, mean zero  $\theta(z^{-1})$  = moving average coefficients  $\phi(z^{-1})$  = auto-regressive coefficients The minimum variance controller used for this project is derived below, following a method given by McGregor [51].

The objective of the MVC is to adjust the process input to exactly offset the effects of any process disturbances and keep  $Y_t = 0$ . This can be done by setting the effect of the compensation equal to the negative of the effect of the disturbance:

$$\frac{\omega(z^{-1})}{\delta(z-1)} U_{t-f-1} = -N_t$$
 (A-3)

to give a control action at time t of

$$U_{t} = -\frac{\delta(z^{-1})}{\omega(z^{-1})} N_{t+f+1}$$
 (A-4)

This control action is obviously not physically realizable, since it requires knowledge of future shocks which are not known at time t. Rather than using the actual shock, the minimum variance forecast of the disturbance,  $\hat{N}_{t+k}$ , is used instead.

The minimum mean square error (MMSE) disturbance prediction is determined as follows. The rational polynomial of the general future shock (k steps in the future),

$$N_{t+k} = \frac{\theta(z^{-1})}{\phi(z^{-1})} a_{t+k}$$
 (A-5)

can be expanded and divided into known and unknown parts.

$$N_{t+k} = (1 + a_1 z^{-1} + a_2 z^{-2} + a_3 z^{-3} + \dots) a_{t+k}$$
  
=  $\psi_1(z^{-1}) a_{t+k} + \psi_2(z^{-1}) a_t$  (A-6)

 $\psi_1(z^{-1}) a_{t+k}$  contains k terms, the unknown future shocks.  $\psi_2(z^{-1}) a_t$  is an infinite series containing present and past shocks. The MMSE estimate of  $N_{t+k}$  at time t is calculated using the known shock information [52].

$$\hat{N}_{t+k/t} = \psi_2(z^{-1}) a_t$$
 (A-7)

The error in the prediction is formed by the future shocks

$$e_{t+k/t} = \psi_1(z^{-1}) a_{t+k}$$
 (A-8)

It can be seen that as the number of periods of dead time increase, the number of terms in (A-8) increases and the error in the forecast becomes larger.

The MMSE prediction (A-7) is an infinite series, which can be represented as a rational polynomial to make it easier to manipulate. A rational expression of  $\psi_2(z^{-1})$ 

$$\Psi_2(z^{-1}) = \frac{T(z^{-1})}{\phi(z^{-1})}$$
 (A-9)

is substituted into the expression obtained by equating the expressions of the future shock in (A-5) and (A-6).

$$\frac{\theta(z^{-1})}{\phi(z^{-1})} = \psi_1(z^{-1}) + \frac{T(z^{-1})z^{-k}}{\phi(z^{-1})}$$

$$\psi_1(z^{-1}) = \psi_1(z^{-1})\phi(z^{-1}) - T(z^{-1})z^{-k}$$
(A-10)

 $T(z^{-1})$  is obtained by equating coefficients, giving the MMSE prediction as a rational polynomial.

The controller is formed from (A-4) using the k step ahead prediction (A-7) instead of the actual disturbance

$$U_{t} = -\frac{\delta(z^{-1})}{\omega(z^{-1})} \hat{N}_{t+k/t}$$

$$= -\frac{\delta(z^{-1})}{\omega(z^{-1})} \cdot \frac{T(z^{-1})}{\phi(z^{-1})} a_{t}$$
(A-11)

Using this MMSE forecast to calculate the control action, the process deviation is given by the prediction error (A-8).

$$Y_{t+f+1} = \psi_{1}(z^{-1})a_{t+f+1}$$

$$\downarrow$$
(A-12)
$$a_{t} = \frac{1}{\psi_{1}(z^{-1})}Y_{t}$$

Using (A-12) to eliminate a, from (A-11), the general minimum variance controller equation is

$$U_{t} = -\frac{\delta(z^{-1})}{\omega(z^{-1})} \cdot \frac{T(z^{-1})}{\phi(z^{-1})} \cdot \frac{1}{\psi_{1}(z^{-1})} \cdot Y_{t}$$
(A-13)

For this project, the process model employed is first order with two gain terms, allowing modelling of fractional periods of dead time:

$$\delta(z^{-1}) = 1 - \delta z^{-1}$$
 (A-14)

$$\omega(z^{-1}) = \omega_0 + \omega_1 z^{-1}$$
 (A-15)

while the noise model has a first order integrating moving average structure:

$$\theta(z^{-1}) = 1 - \theta z^{-1}$$
 (A-16)

A-4

A-5

$$\phi(z^{-1}) = 1 - z^{-1} \tag{A-17}$$

Two whole periods of dead time were used, so f=2 (and k=3, including one period of zero order hold).

When the noise model is expanded as in (A-6),

$$N_{t+3} = 1 + (1-\theta)z^{-1} + (1-\theta)z^{-2} + (1-\theta)z^{-3} + \dots$$
 (A-18)

and

$$\Psi_1(z^{-1}) = 1 + (1-\theta)z^{-1} + (1-\theta)z^{-2}$$
 (A-19)

$$\psi_2(z^{-1}) = (1-\theta) + (1-\theta)z^{-1} + (1-\theta)z^{-2} + \dots$$
 (A-20)

These expressions are substituted into (A-10) and  $T(z^{-1})$  is found to be

$$T(z^{-1}) = (1-\theta)$$
 (A-21)

- - 2

All of these expressions are substituted into the controller equation (A-13). The final form of the minimum variance controller is

$$u_{t} = -\frac{1-\delta z^{-1}}{\omega_{0}+\omega_{1}z^{-1}} \cdot \frac{1-\theta}{1-z^{-1}} \cdot \frac{1}{1+(1-\theta)z^{-1}+(1-\theta)z^{-2}} \cdot \eta_{t}$$
 (A-22)

where  $u_t$  and  $\eta_t$  are the peroxide concentration and the process viscosity in deviation form (see chapter 7). Recalling that  $\Delta = 1 \cdot z^{-1}$ , the more useful velocity form of the controller is

.

$$\Delta u_{t} = -\frac{1-\delta z^{-1}}{\omega_{0}+\omega_{1}z^{-1}} \cdot (1-\theta) \cdot \frac{1}{1+(1-\theta)z^{-1}+(1-\theta)z^{-2}} \cdot \eta_{t}$$
 (A-23)

The BASIC language coding of this equation is

$$DU = ((W1-A^*W0)^*DUTM1 + (A^*W1-A^*W0)^*DUTM2 + (A-24)$$
  
A^\*W1^\*DUTM3 + A^\*(VISC-D^\*VISCTM1)) / W0

where DU is the control action, DUTM1-3 are the three past control actions, VISC is the current viscosity in deviation form and VISCTM1 is the previous viscosity. W1, W0 and D correspond to  $\omega_1$ ,  $\omega_0$  and  $\delta$ , while A is (1- $\theta$ ).

### A.2 Process Model Identification

Process and noise models were fit to experimental data using a software package called MATLAB (version 3.5f). This appendix outlines the procedure used to fit discrete models, and mentions the major MATLAB subroutines that were used. One comment on notation; for the polynomial in the process model denominator, MacGregor [51] defines  $\delta(z^{-1}) = 1 - \delta_1 z^{-1} - \delta_2 z^{-2} - ...$  so that the  $\delta_i$  values are positive, whereas MATLAB uses  $F(z^{-1}) = 1 + F_1 z^{-1} + F_2 z^{-2} + ...$  and produces negative coefficients. MacGregor's notation is used herein, so that the actual coefficients determined by MATLAB differ from those reported for  $\delta(z^{-1})$  by a minus sign. The same comment applies to the  $\theta(z^{-1})$  function in the noise model.

### 1. Raw Data Preprocessing

The first step is to read the raw process data, from a PRBS or other identification experiment, into the MATLAB operating environment as two vectors (or lists) of information. The variables of importance are the process input (the peroxide concentration) and the process output (the measured viscosity). The DTREND routine is used to remove the mean value from each vector, effectively putting the data into deviation variable format. A MATLAB routine called IDPLOT may be used to view the raw data. A sample PRBS identification test is used to illustrate the identification procedure; the raw data are displayed in Figure A-1 in a fashion similar to the IDPLOT output.

### 2. Determining the form of the process model

The first time through the analysis, the specific form of the process model must be determined. The general form of the process model is

$$\eta(t) = \frac{\omega(z^{-1})}{\delta(z^{-1})} u(t-f-1)$$
 (A-24)

ŝ



Figure A-1 - Process data for a sample analysis, with the peroxide concentration as the manipulated input, and viscosity at 30 1/s as the measured response. Data sampling period  $\Delta t = 25s$ .

The number of terms in the polynomials  $\omega(z^{-1})$  and  $\delta(z^{-1})$ , and the number of whole sample periods of dead time f, must be determined. For simple processes with a single input and output, the easiest procedure is trial and error. Vary the number of terms in the  $\delta$  and  $\omega$  functions, as well as the number of periods of dead time f, and fit the data to each model. Using MATLAB on an IBM PC computer with a 486DX processor, fitting a model to the data takes less than one minute. Examine the loss function to determine how well each model fits; the lower the value, the better the model fits. Compare the values of the parameters with the estimated values of their standard deviations to ensure that they are significant. In most cases, increasing the number of parameters quickly leads to diminishing improvements in the fit. The

A-8

value of the loss function levels out, or decreases only very slightly as the model becomes more complex. The model with the fewest parameters that gives an acceptable fit should be selected. MATLAB has two routines, ARCSTRUC and IVSTRUC which help accomplish this step in the analysis. If two forms of the model have similar results, carry them both through the later stages of the analysis and then determine which fits the data better.

Using this methodology, it was found that the best model structure for this process, with  $\Delta t = 25$ s, was

$$\omega(z^{-1}) = \omega_0 + \omega_1 z^{-1}$$
  
 $\delta(z^{-1}) = 1 - \delta_1 z^{-1}$  (A-25)  
 $f = 2 \text{ periods}$ 

or two coefficients for  $\omega(z^{-1})$ , one coefficient for  $\delta(z^{-1})$ , and two full periods of dead time. This form is equivalent to a first order plus dead time model in the continuous domain.

The same methodology may be used to obtain a noise model. In this case, Palmor and Shinnar [47] suggest that a first order integrating noise model of the form

$$N(t) = \frac{1 - \theta z^{-1}}{1 - z^{-1}} a(t)$$
 (A-26)

10 1

where a(t) is a white noise generator and  $\theta$  is a single coefficient, should be sufficient. Increasing the number of parameters in the numerator and denominator of equation (A-26) did not result in any significant improvements in the model.

Once the structure of the model has been determined for the system, it is not necessary to repeat this procedure unless there is a radical change in the process. Examining the residuals of the model, as explained in the next steps, will alert the analyst if this is the case.

### 3. Fitting the process model

Once the form of the process model is known, the next step is to fit the parameters of the model to the data. There are a number of routines available in MATLAB to assist with this, depending on the chosen model. The output error (OE) routine can be used to fit equation (A-24) without attempting to fit a noise model. If examination of the residuals indicates that a noise model is required, then the more general prediction-error method routine (PEM) is used (step 4).

To continue the analysis of the data presented in Figure A-1 using the model structure determined in step 2, the OE routine is used to generate the coefficients

	Value	Std Dev.
ω	-0.53	0.06
ω	0.28	0.06
δ	-0.94	0.01

**Table 9-1** - Results of fitting process model in equation (A-24) to data in Figure A-1 using OE routine.

presented in Table 9-1. Predicted data can then be compared with the actual data to see how well the model fits; the RESID routine is used to generate and analyze residuals (the difference between a data point and the value that the model predicts). Two correlations are performed and displayed by resid:

i) The top graph in Figure A-2 shows the auto-correlation function of the residuals. If the residuals are random noise, the function will be zero; any significant values (outside the  $3\sigma$  confidence interval about zero) indicate that the residuals are not random and should be modelled. In this case, the function is non-zero before lag six; a noise model should be employed.

ii) A cross-correlation between the process input (peroxide concentration) and the residuals is displayed in the lower graph of Figure A-2. This demonstrates how



Figure A-2 - Two graphs generated by the RESID function. The first is the auto-correlation function of the residuals. The second is a cross-correlation between the residuals and the process input.

well the model fits by revealing any correlation between the process input and output not accounted for by the model. If the results are non-zero (i.e. outside the  $3\sigma$ confidence limits) at any lag, then the model structure should be re-examined (back to step 2). Here, we can see that the model fits the data fairly well. The points at  $\pm 3$  lags are just at the lower confidence limit, indicating that there may be a marginally significant correlation at 3 periods.

## 4. Including the noise model

If correlated noise is present, the general prediction-error method routine PEM can be used to fit the combined process and noise model used in this study:

A-12

$$\eta(t) = \frac{\omega_0 + \omega_1 z^{-1}}{1 - \delta z^{-1}} u(t - f - 1) + \frac{1 - \theta z^{-1}}{1 - z^{-1}} a(t)$$
 (A-27)

	Values	Std Dev.
ω <sub>0</sub>	-0.44	0.03
ω <sub>1</sub>	-0.26	0.05
δ	-0.21	0.08
θ	-0.61	0.09

Table 9-2 - Results of using PEM to fit data to equation (A-27).

The coefficients obtained when this model is fit to the data from Figure A-1 are displayed in Table 9-2. The analysis of the residuals is shown in Figure A-3. The addition of the noise model has removed the auto-correlation from the residuals and has improved the fit and stability of the process model, as will be explained below.

### 5. Stability and invertibility

The last check to perform on a model is ensure that it is both stable and invertible. A model is considered stable if, for any bounded input, it products a bounded output. The stability of a model can be determined by examining the location of its poles on the complex plane.

The poles of the process model are the values of z which cause the model response to become infinite; in this case, the roots of the polynomial  $\delta(z^{-1})$ , which cause the denominator of the model to be zero. As z approaches one of the roots, the model response becomes asymptotic, hence the term "pole". Since  $\delta(z^{-1})$  may be quadratic or higher, the roots of  $\delta(z^{-1})$  may be complex. A model is stable its poles all fall within a unit circle about the origin on the complex plane; i.e. the magnitude



Figure A-3 - Auto and cross correlation functions generated by the RESID function for the process and noise model parameters generated by PEM. The dotted lines mark the  $3\sigma$  confidence intervals about zero.

of the complex roots must be less than or equal to one.

When the process model is incorporated into a minimum variance controller, it is inverted and used to predict input values given an output value. The model must be stable when inverted as well as in forward form. When a model is inverted, the numerator and denominator switch positions. The "zeros" of the process model (the roots of the numerator,  $\omega(z^{-1})$ ) become the poles of the inverted model. Thus, if the zeros and poles of a process model all have a magnitude less than one, the model is both stable and invertible.

In this case, the poles and zeros of the model are easy to determine by inspection, since the numerator and denominator are linear polynomials; the roots fall on the real axis. For the OE process model (Table 9-1), there is a zero at z=0.5235 and a pole at z=0.9357. Since the absolute values of the roots are less than one, the model is stable and invertible. For the full model incorporating the noise model (Table 9-2), the zero is at z=-0.5978 while the pole is at z=0.2091; again the model is stable and invertible. However, notice that the magnitude of the pole is lower for the full model; including the noise model has improved the stability of the process model by moving the pole closer to the origin.

:

# **APPENDIX B**

# SAMPLE *BASIC* PROGRAMS, SST CALIBRATION CALCULATIONS

### APPENDIX B

### Sample Control Programs: Source Codes

#### Minimum Variance Control Program

#### Main Program VSTEP2.BAS

```
'PROGRAM VSTEP2.BAS --AUTHOR: BURKE NELSON
'$INCLUDE: 'MACODEC.BAS'
'SINCLUDE: 'DT2-1DEC.BAS'
'SINCLUDE: 'GRAPHDEC.BAS'
DECLARE SUB SETSCRN (F$)
DECLARE FUNCTION INPUTSTR$ ()
DECLARE FUNCTION ATTNMENU% ()
DECLARE SUB RHEO.FLSH ()
DECLARE SUB RHEO.MMT ()
DECLARE SUB RHEO.INIT ()
DECLARE SUB RHEO.SPT (SR!)
DECLARE SUB CHANSAMP (B%())
CONST TS = 25
                    'SAMPLE PERIOD
CONST TMT = 1
                     'TEST MEASUREMENT TIME BEFORE SAMPLING
                    'LENGTH OF HIGH SHEAR RATE FLUSH
CONST TFLUSH = 12
CONST TRENEW = 4
CONST CP = 1
CONST W0 = -.43
CONST W1 = .25
CONST D = .2278
CONST A = 1 - .6
CONST SSTCAL = 14966 'SST CALIBRATION CONSTANT, Pa/V
CONST TREF = 200 'REFERENCE TEMPERATURE FOR VISCOSITY
CONST EA = 5700
                     'ACTIVATION ENERGY FOR VISC. TEMP.
                     ADJUSTMENT
CONST R = 8.31385
                     'IDEAL GAS LAW CONSTANT
                    'TEMP CALIBRATION DEGREES PER VOLT
CONST TCAL1 = 5
                    'TEMP CALIBRATION CONSTANT
CONST TCAL2 = 175
CONST H = .001
                     'GAP SIZE
CONST L = .0516 'LENGTH OF GAP
CONST YSTAR = .000475
                         'Y* VALUE FOR VISCOSITY CORRECTION
CONST PISLP = 92.46
CONST P1CON = -63 'CONST. FOR PRESSURE ZONE CALIBRATIONS
CONST P2SLP = 91.21 '(VOLTAGE TO PSI CONVERSION)
CONST P2CON = -49
```

```
'NUMBER OF SAMPLES PER CHANNEL PER
CONST NSAMP = 36
                     MEASUREMENT
                    'NUMBER OF SAMPLES FOR BASELINE
CONST NBSAMP = 54
CONST NCONVT = 409.6 * NSAMP 'CONV. FACTOR FOR AVG CALCS
CONST NECONVT = 409.6 * \text{NBSAMP}
CONST RECSIZE = NSAMP * 8 'RECORD SIZE FOR RAW DATA FILE
CONST PSI2PA = 101325 / 14.7 'CONST. FOR PSI TO PA CONV.
MBCN = 1000
             'MASTERBATCH CONC. IN PPM (NOT CONSTANT)
                         'AXIS TITLES FOR ONLINE GRAPHING
DIM T$(2), U$(1), DB(3)
T$(0) = "INLINE PROCESS VISCOSITY MEASUREMENTS"
T$(1) = "TIME (s)"
T$(2) = "VISCOSITY (Pa s)"
U$(0) = "######"
U$(1) = "#######"
CLS
PRINT "PROCESS VISCOSITY CONTROL AND DATA COLLECTION PROGRAM
(MVC CONTROLLER)"
INPUT "VISCOSITY DATA FILE NAME"; F$
FR$ = F$ + ".DAT"
F$ = F$ + ".MAT"
INPUT "DESIRED SHEAR RATE"; DSR
INPUT "TOTAL RUN TIME (s)"; TOT
NTOT = INT(TOT / TS) + 1
                       'DECLARE MAIN DATA ARRAY
DIM RDATA (NTOT%, 10)
MACO.INIT 1, 1, -1
DT.INIT
RHEO.INIT
FREQ = 25000
                        'SET FREQ VERY HIGH SO SAMPLES
                         CLOSE TOGETHER IN TIME
DT.CLOCK FREQ
                       'SAMPLE EACH CHANNEL ONCE
DT.SETADC 1, 0, 4, 5
DIM B(4, NBSAMP), BA(4), V(4, NSAMP), VA(4)
INPUT "INITIAL CONTROLLER SETPOINT (Pa s)"; CVSPT
INPUT "INITIAL PEROXIDE CONCENTRATION"; PPM
INPUT "NUMBER OF CONTROL PERIODS BEFORE CONTROLLER KICKS
IN"; NTC%
NTC = NTC * CP
INPUT "CONTROL PERIOD NUMBER OF FIRST PROCESS STEP (s)";
NTSTEP*
NTSTEP_{*} = NTSTEP_{*} * CP
PRINT "ENTER NEW VISCOSITY, FEED SETPOINTS FOR THE PROCESS
STEP"
INPUT "TOTAL FEED RATE (KG/H)"; FTOT
INPUT "NEW VISCOSITY SETPOINT (Pa s)"; NVSPT
PTXT = 1
                  'ALLOW PRINTING OF DATA TO THE SCREEN
SETSCRN FS
OPEN "O", 3, F$
                            'OPEN MAIN DATA FILE
```

**B-2** 

OPEN "R", 2, FR\$, RECSIZE 'OPEN RAW DATA FILE DIM BLREC AS STRING \* RECSIZE, MLREC AS STRING \* RECSIZE LOCATE 10, 30: INPUT "HIT ENTER TO START"; A1\$ COUNT = 0 CLS TIMER ON ON TIMER(TS) GOSUB COLLECT T = TIMER + TMT + NBSAMP / 18 GOSUB COLLECT XXWAIT: 'WAIT FOR AN INSTRUCTION OR MEASUREMENT Z\$ = ""DO ZS = INKEYSLOOP UNTIL Z = "!" OR TIMER - T > TOT MENU: PTXT = 0 IF Z = "!" THEN ON ATTNMENU% GOTO STEPCHG, RESGRAPH, DISPLAY, PROGEXIT END IF **PROGEXIT:** CLOSE PRINT PRINT TAB(35); "FINISHED" VIEW PRINT CLS END COLLECT: SR = 0RHEO.SPT SR CHANSAMP B%() 'GET BASELINE MEASUREMENT SR = DSR'START SHAFT TURNING RHEO.SPT SR T4 = TIMER'GET PROCESS VALUES FROM THE MACO MACO.OPEN MACO.VAL "T2V1", TRHEO%, MERR% MACO.VAL "T2V6", TMELT%, MERR% MACO.VAL "DRV2", FDR1%, MERR% MACO.VAL "DRV3", FDR2%, MERR% MACO.CLOSE ERASE BA, VA BLINE\$ = "" FOR  $I_{\delta} = 0$  TO NBSAMP - 1 'BASELINE AVERAGES FOR  $J^* = 0$  TO 3  $BA(J_{*}) = BA(J_{*}) + B_{*}(J_{*}, I_{*})$ BLINE = BLINE + MKI (B (J , I )) NEXT J% NEXT I%

÷.,

```
BLREC = BLINES
                               'STORE RAW BASELINE DATA
   PUT #2, BLREC
   P1B = P1SLP * BA(2) / NBCONVT + P1CON
                                            'BASELINE PRESS.
   P2B = P2SLP * BA(3) / NBCONVT + P2CON
   PB = (P1B + P2B) / 2
   DPB = P1B - P2B
   DO
                                     WAIT UNTIL STEADY STATE
   LOOP UNTIL TIMER - T4 > TMT
,
                                      REACHED
                                'OFFICIAL TIME OF MEASUREMENT
   TM = TIMER - T
                                'READ IN MEASUREMENT DATA
   CHANSAMP V<sup>()</sup></sup>
                                'TIMER TO END FLUSH
   TFLUSH1 = TIMER + TFLUSH
   SR = 30
   RHEO.FLSH
                     'HIGH SHEAR RATE FLUSH WHILE PROCESSING
   RHEO.SPT SR
   MLINES = ""
                                'MEASUREMENT AVERAGES
   FOR I_{*}^{*} = 0 TO NSAMP - 1
      FOR J_{\pi}^{*} = 0 TO 3
         VA(J_{*}) = VA(J_{*}) + V_{*}(J_{*}, I_{*})
         MLINE\$ = MLINE\$ + MKI\$(V\$(J\$, I\$))
      NEXT J%
         VA(4) = VA(4) + V^{*}(4, I^{*})
REM
   NEXT I%
   MLREC = MLINE$
                                'STORE RAW MEASUREMENT DATA
   PUT #2, MLREC
   P1M = P1SLP * VA(2) / NCONVT + P1CON 'MEASUREMENT PRESS.
P2M = P2SLP * VA(3) / NCONVT + P2CON
   PM = (P1M + P2M) / 2
   DPM = P1M - P2M
   DP = ABS(DPM) * PSI2PA * 38 / 66
                                           'CONVERT TO Pa FOR
                                            USE IN FORMULA
REM RTEMP = VA(4) / NCONVT * TCAL1 + TCAL2 'MEASUREMENT TEMP
   STRESS = (VA(0) / NCONVT - BA(0) / NBCONVT) * SSTCAL + 37
* DPB + 11 * (PM - PB)
   SVEL = (3.32309 * VA(1) / NCONVT - .31235) * H
   VISC = (STRESS - DP / L * H / 2) / SVEL * H
REM VISC = VISC * EXP(EA / R * (1 / (TREF + 273) - 1 / 
(RTEMP + 273))
   SR = SVEL / H * (STRESS * L - DP * YSTAR) / (STRESS * L -
DP * H / 2)
   IF COUNT = NTSTEP THEN CVSPT = NVSPT
   IF (COUNT% MOD CP = 0) AND (COUNT% > NTC%) THEN GOSUB
CONTROL
                         'LIST TO SCREEN
   IF PTXT_{3} = 1 THEN
      IF FLGSTAR% THEN
          PRINT USING "####"; COUNT% / CP;
         FLGSTAR = 0
      ELSE
         PRINT "
                    · ** ;
      END IF
      PRINT USING " ######.# "; TM;
      PRINT USING " ###.## "; FDR1% / 100; FDR2% / 100;
```

```
####"; CVSPT;
      PRINT USING "
                        ####.#"; PPM;
      PRINT USING "
      PRINT USING "
                       ####.# "; TRHEO%;
                       #### "; TMELT%;
      PRINT USING "
      PRINT USING "###.## "; SR;
      PRINT USING "######.#"; VISC
   END IF
   RDATA(COUNT<sup>*</sup>, 0) = TM
   RDATA(COUNT*, 1) = FDR1* / 100
   RDATA(COUNT<sup>*</sup>, 2) = FDR2<sup>*</sup> / 100
   RDATA(COUNT*, 3) = PM
   RDATA(COUNT<sup>*</sup>, 4) = DPM
   RDATA(COUNT<sup>*</sup>, 5) = TRHEO<sup>*</sup>
   RDATA(COUNT<sup>*</sup>, 6) = TMELT<sup>*</sup>
   RDATA(COUNT*, 7) = SR
   RDATA(COUNT*, 8) = VISC
   RDATA(COUNT<sup>*</sup>, 9) = PPM
   RDATA(COUNT%, 10) = CVSPT
   FOR J_{*}^{*} = 0 TO 10
      PRINT #3, RDATA(COUNT%, J%);
   NEXT J%
   PRINT #3,
   COUNT = COUNT + 1
   DO
   LOOP UNTIL TIMER > TFLUSH1 'TIMER FOR HIGH RATE FLUSH
   TNEW = TIMER + TRENEW
   RHEO.MMT
   SR = 30
   RHEO.SPT SR
   DO
   LOOP UNTIL TIMER > TNEW
                                 'TIMER FOR SAMPLE RENEWAL
   SR = 0
   RHEO.SPT SR
RETURN
STEPCHG:
CLS
PRINT "CURRENT TIME:"; TIMER - T; "s"
PRINT
PRINT "SAMPLE PERIOD NUMBER OF PROCESS STEP (s) ? ";
A1\$ = INPUTSTR\$: NTSTEP\$ = VAL(A1\$) * CP
IF TIMER - T > NTSTEP% * TS THEN PRINT "TOO LATE": GOTO MENU
PRINT "ENTER NEW PROCESS SETPOINTS FOR THE PROCESS STEP"
DO
   PRINT "TOTAL FEED RATE (KG/H) ? ";
   FTOT = VAL(INPUTSTR$)
   PRINT "NEW VISCOSITY SETPOINT (Pa·s)? ";
   NVSPT = VAL(INPUTSTR$)
   PRINT "SETPOINTS CORRECT (Y/N)";
   A1\$ = INPUTSTR\$
LOOP UNTIL UCASE$(A1$) <> "N"
GOTO MENU
```

B-5

```
DISPLAY:
SETSCRN F$
               'SET FLAG TO ALLOW PRINTING TO THE SCREEN
PTXT = 1
GOTO XXWAIT
RESGRAPH:
CLS
VIEW PRINT
DCNT% = COUNT% - 1 ' FREEZE COUNT SO DOESN'T CHANGE WHILE
GRAPHING
DI\% = 0
                     ' SHOW ALL DATA
IF DI% > DCNT% - 2 GOTO MENU 'NOT ENOUGH POINTS TO GRAPH
REDIM DX(DI% TO DCNT%), DY(DI% TO DCNT%), DS(DI% TO DCNT%)
                              'SET MAX, MIN AXIS VALUES
DXMIN = RDATA(DI<sup>*</sup>, 0)
DXMAX = RDATA(DCNT^{*}, 0)
                               'PUT DATA INTO ARRAYS TO GRAPH
DYMIN = 1E+16
DYMAX = 0
FOR DI1 = DI TO DCNT
   DX(DI1\%) = RDATA(DI1\%, 0)
   DY(DI1\%) = RDATA(DI1\%, 8)
   DS(DI1\%) = RDATA(DI1\%, 10)
   IF DY(DI1\%) > DYMAX THEN DYMAX = DY(DI1\%)
     ELSE IF DY(DI1\%) < DYMIN THEN DYMIN = DY(DI1\%)
   IF DS(DI1\%) > DYMAX THEN DYMAX = DS(DI1\%)
     ELSE IF DS(DI1\%) < DYMIN THEN DYMIN = DS(DI1\%)
NEXT DI1%
DB(0) = INT(DXMIN)
DB(1) = INT(DXMAX + .5)
DB(2) = INT(DYMIN)
DB(3) = INT(DYMAX) + 1
INITGRAPH T$(), DB(), U$()
ADDLINE DX(), DY()
ADDLINE DX(), DS()
DO
LOOP UNTIL INKEY$ <> ""
RESETGRAPH
GOTO MENU
CONTROL:
                'FLAG TO PRINT # ON SCREEN (INDICATES CON-
FLGSTAR_{*}^{*} = -1
TROL ACTION)
' MVC CONTROLLER WITH GAIN SCHEDULING
VERR = CVSPT - VISC
GAIN = VISC / 627.2 - .42314
DPPM = ((W1 - A * W0) * DPPM1 + (A * W1 - A * W0) * DPPM2 +
A * W1 * DPPM3 + A * (VERR - D * VERRM1)) / (WO * GAIN)
PPM = PPM + DPPM
DPPM3 = DPPM2
DPPM2 = DPPM1
DPPM1 = DPPM * GAIN
VERRM1 = VERR
IF PPM < 0 THEN PPM = 0
```

```
IF PPM > MBCN THEN PPM = MBCN
F1 = (1 - PPM / MBCN) * FTOT
F2 = (PPM / MBCN) * FTOT
IF F1 <= 1 THEN F1S = 0 ELSE F1S = 1
IF F2 \leq 1 THEN F2S% = 0 ELSE F2S% = 1
IF F1 > 0 THEN SFDR1% = INT(F1 * 100 + .5) 'CONVERT FOR MACO
IF F_2 > 0 THEN SFDR2% = INT(F<sub>2</sub> * 100 + .5)
MACO.OPEN
DO
MACO.SET "DRS2", SFDR1%, MERR% 'SET SETPOINT VALUES
LOOP UNTIL MERR = 0
DO
MACO.SET "DRS3", SFDR2%, MERR%
LOOP UNTIL MERR = 0
DO
MACO.W.OPCR 2704, F1S%, MERR%
                                   'ENABLE/DISABLE FEEDERS
LOOP UNTIL MERR = 0
DO
MACO.W.OPCR 2705, F2S%, MERR%
LOOP UNTIL MERR = 0
MACO.CLOSE
RETURN
END
FUNCTION ATTNMENU%
VIEW PRINT
CLS
LOCATE 8, 32
PRINT "ATTENTION MENU"
PRINT TAB(25); "1) ENTER SETPOINT CHANGE"
PRINT TAB(25); "2) RESULTS GRAPH"
PRINT TAB(25); "3) RETURN TO DISPLAY"
PRINT TAB(25); "4) EXIT AND SAVE DATA"
DO
   PRINT TAB(25); "ENTER SELECTION:";
   A1\$ = INPUTSTR\$: A1\$ = VAL(A1\$)
LOOP UNTIL A1 > 0 AND A1 < 5
ATTNMENU = A1%
END FUNCTION
FUNCTION INPUTSTR$
A1\$ = INKEY\$
A1$ = ""
S$ = ""
PS_{\ast} = POS(0)
CS = CSRLIN
\mathbf{P}^{\ast} = \mathbf{0}
DO WHILE A1$ <> CHR$(13)
   DO
      A1\$ = INKEY\$
   LOOP UNTIL A1$ <> ""
```

```
SELECT CASE ASC(A1$)
      CASE 32 TO 127
         PRINT A1$;
         S$ = S$ + A1$
         P_{*} = P_{*} + 1
      CASE 8
         IF P% > 0 THEN
            S = LEFT$(S$, LEN(S$) - 1)
            P_{*}^{*} = P_{*}^{*} - 1
            LOCATE CS%, PS% + P%
            PRINT " ";
            LOCATE CS%, PS% + P%
         END IF
      CASE 13
         PRINT
   END SELECT
LOOP
INPUTSTR$ = S$
END FUNCTION
SUB SETSCRN (F$)
CLS
VIEW PRINT
              TIME FDR 1 FDR 2
                                      Vspt CONC'N
PRINT "####
                         VISC"
      MELT SR
RHEO.
PRINT STRING$(80, "=")
LOCATE 23, 1
PRINT STRING$(80, "=")
PRINT "HIT <!> FOR MENU", , , " FILE: "; F$;
VIEW PRINT 3 TO 22
END SUB
Subroutine CHANSAMP
DECLARE SUB DT.DMAADC (D%(), ABOUND%)
DECLARE SUB DT.DMAWAIT (D%(), ELEMENT%)
DECLARE FUNCTION DT.DMALEN% (D%())
SUB CHANSAMP (B%())
LB1 = LBOUND(B, 1)
UB1 = UBOUND(B, 1)
LB2 = LBOUND(B, 2)
UB2 = UBOUND(B, 2)
```

```
DIM D%(LB1% TO UB1%)

A% = 0

FOR I% = LB2% TO UB2%

T = TIMER

DT.DMAADC D%(), A%

DT.DMAWAIT D%(), UB1%

FOR J% = LB1% TO UB1%
```

10

**B-8** 

```
B%(J%, I%) = D%(J%)
NEXT J%
DO
LOOP UNTIL TIMER > T
NEXT I%
END SUB
```

### Subroutine RHEO.SPT

```
DECLARE SUB DT.DAOUT (DAC.CHAN%, VALUE%)
SUB RHEO.SPT (SR)
'SET THE RHEO. DRIVE MOTOR AT A CERTAIN SHEAR RATE
' SR RETURNS WITH THE ACTUAL SHEAR RATE SENT TO THE DRIVE
CONTROLLER
' DRIVE SET TO RUN FROM DAC 1
IF SR <> 0 THEN
   RPM = ABS(SR / 2.618)
  V% = INT((.0064904 * RPM ^ 3 - .10293 * RPM ^ 2 + 1.1115
* RPM - .37122) * 409.6 + .5)
   DT.DAOUT 1, V%
   VOLT = V% / 409.6
   SR = 2.618 * (-.0093319 * VOLT ^ 3 + .085228 * VOLT ^ 2 +
1.3125 * VOLT - .068211)
ELSE
   DT.DAOUT 1, 0
END IF
END SUB
```

### **SST Calibration Calculations**

The shear stress transducer was calibrated using known weights to simulate a shear force. Wires were attached to the SST beam above the disk spring and run through calibration ports in the housing (see figure B-1, figure 2-4). The wire was run over an air bearing so that the weights could hang vertically. When performing a calibration, the weights were hung so as to approach their steady state position from above and below, removing any systematic error due to friction in the air bearing.

The weight attached to the wire provides a force  $F_w$  on the beam, at the



Figure B-1 - Geometry of the beam for calibration

calibration point C. In Figure B-1, the disk spring is the pivot point on the beam and is defined as point B, while and the active face is point A. The lengths are  $L_{AB}$ = 30 mm and  $L_{BC}$ = 25 mm.  $F_w$  will cause the beam to move, with the capacitance probe at point D measuring the amount of deflection and producing a signal from the SST.

The force  $F_w$  must be related to the shear stresses at point A. Since the beam is free to pivot, a simple ratio of the lever arms can be used:

$$F_A = \frac{L_{BC}}{L_{AB}} F_w$$

Substituting in the actual lengths and using  $F_w = 9.81 M_{cal}$ , where  $M_{cal}$  is the mass of the suspended weight in kg, gives  $F_A$  in N:

$$F_{A} = \frac{25}{30} \cdot 9.81 \ M_{cal} = 8.175 \ M_{cal}$$

Converting the force into a shear stress at the face simply requires dividing through by the area of the 8 mm diameter active face:

$$\sigma_{A} = \frac{F_{A}}{\frac{\pi}{4} 0.008^{2}} = 1.99 \times 10^{4} F_{A}$$

and the shear stress  $\sigma_A$  is related to the calibration weight by:

$$\sigma_{\rm A} = 1.626 \times 10^5 M_{\rm cal}$$

A typical calibration would involve hanging several weights to simulate a range of stresses, recording the SST signal for each weight. Weights up to 100 g were used, since this simulated stresses over the range encountered while operating. Linear regression was used to fit a line through the results to get SST voltage as a function of shear stress. The slope of this line was the calibration constant, in Pa/V. A typical result is shown in figure 2-5.

1

# **APPENDIX C**

# **DETAILED RHEOMETER DRAWINGS**

Drawings by F.R. Bubic

.

,



.



GROPHIC SCALE

34

18 2.8

......

40 58 68 18

EXTRUDER

Al main

.....

.

TOP VIEW OF RHEOMETER WITH SHAFT IN PLACE

ß

R

×

DATE: Jal 22/10 DRAWING No:

BY: LE Babic

88522B



**C**2

## DRIVE SHAFT DETAIL









C5

TORSION BAR SHEAR STRESS TRANSDUCER - CONCEPT



**C6**
# DISK SPRING SHEAR STRESS TRANSDUCER



• • •

**C**7

# **APPENDIX D**

# EQUIPMENT AND PEROXIDE SPECIFICATIONS

#### WAVEFORMS (FUNCTIONS)

DC, square, triangle, up-ramp, downramp, sine, cosine, inverse sine, and haversine waveforms are provided. Each of these waveforms can be stored into the waveform memory between thumbtacks automatically, and then edited with the waveform editing functions if desired.

#### **OPERATIONAL MODES**

#### Continuous

Output runs repetitively from the programmed start address to the programmed stop address.

#### Triggered

Output quiescent until triggered by external signal or front panel pushbutton, then runs until another break point is encountered. Break points can be inserted anywhere in the waveform with the default break point at the beginning of the waveform.

#### Gated

Same as triggered mode except that the output is continuous for the duration of the gate signal and until the first break point encountered after the gate signal ends.

#### Burst

Same as in the triggered mode except that a programmable number of waveforms is counted before the waveforms stop. The maximum burst is 1,048,575 waveforms.

#### Toggled

The output is quiescent until triggered. It then runs continuously until another trigger stops the waveform at the next break point.

#### WAVEFORM RESOLUTION

#### Normal Waveform

2048 points horizontal  $\times$  4095 points vertical.

#### **Chained Waveform**

8192 points horizontal  $\times$  4095 points vertical. Stored waveforms are not available with chained operation.

# SAMPLE RATE

#### Range

0.02 Hz to 2.0 MHz (50 s to 500 ns).

#### Waveform Period and Frequency

The actual waveform period is the number of horizontal points (from start to stop address) times the sample time. This can range from 1 microsecond for a square wave to 113.8 hours for a waveform using all 8192 points.

# Frequency Resolution

4 digits. Frequency Accuracy

- ±0.015%.
- Repeatability (24 Hr) ± 25 ppm.

Temperature Coefficient

<5 ppm/°C.

## **OUTPUT SIGNALS**

#### Ampiltude

**Range:**  $\pm 0.005$  to 5 Vp into 50 $\Omega$  (0.01 to 10 Vp-p into 50 $\Omega$ ).  $\pm 0.01$  to 10 Vp into an open circuit (0.02 to 20 Vp-p into an open circuit).

Resolution: 3 digits.

Accuracy:  $\pm 1.8\%$  of setting and  $\pm 2.5$  mV for amplitude + offset  $\ge 0.5V$ .

 $\pm$  1.8% of setting and  $\pm$  0.25 mV for 0.5V > amplitude + offset >50 mV.

 $\pm$  1.8% of setting and  $\pm$  25  $\mu$ V for 50 mV > amplitude + offset.

**Repeatability (24 Hr):**  $\pm 0.1\%$  of setting.

Temperature Coefficient: <150 ppm/ 0°C of setting.

#### Offset

**Range:** +5V to -5V into 50Q (-10V to +10V into an open circuit). Absolute amplitude plus offset may not exceed  $\pm 5V$  into 50Q ( $\pm 10V$  into an open circuit).

Resolution: 3 digits.

Accuracy: 2% or setting and  $\pm$  15 mV for amplitude  $\pm$  offset  $\ge$ 0.5V.

2% of setting and  $\pm 1.5 \text{ mV}$  for 0.5V >

amplitude + offset  $\geq$ 50 mV. 2% of setting and ±0.15 mV for 50 mV

> amplitude + offset.

Repeatability (24 Hr): ±5 mV and ±0.1% of setting.

Temperature Coefficient: <1 mV/°C and <150 ppm/°C of setting.

#### OUTPUTS

#### ARB Out (50Q)

Source of primary waveform output. Maximum amplitude is  $\pm 5$  Vp into 50Q. Output is fuse protected.

#### Sync Out (TTL)

Will drive up to 10 LSTTL loads. This is a pulse 1 sample time wide that is usually used to sync an oscilloscope or another ARB generator. Pulse position is adjustable to any point in the waveform.

#### **Burst Done Out (TTL)**

Will drive up to 10 LSTTL loads. A TTL low indicates that the waveform is running. TTL high indicates that the instrument is waiting for a trigger in triggered, gated, toggle, or burst modes. Used primarily to start another ARB generator in series operation.

#### Ref Out (TTL)

Will drive up to 10 LSTTL loads. This pulse train at the sample frequency is used primarily as a reference source for other ARB generators in series operation or in parallel operation.

#### Z-Axis Out

This signal is a pulse, adjustable in amplitude from 2 to 14 volts, that is used to modulate the Z-axis of an oscilloscope when using the waveform editing features. The logic polarity is also selectable.

#### INPUTS

#### Sum In (50Q)

The signal at this input is added to the arbitrary waveform to produce an output (at waveform out) of the sum of the two. A peak input of  $\pm$  5V will produce an output equal to the amplitude setting. Input is fuse protected. Accuracy is 4% (2% if fuse is shorted).

#### Trig In (TTL)

Impedance is 100 KQ. Signal is used to control the generator in the trigger, gate, toggle, and burst modes. Slope polarity is selectable.

#### Sync In (TTL)

. . . .

Impedance is 100 KQ. A high input causes the waveform to restart at the start address. Primarily used for syn-

chronizing several arbitrary waveform generators in parallel operation.

#### Ref In (TTL)

Impedance is  $100 \text{ K}\Omega$ . This signal input is used for the sample clock when the external ref is selected.

# Hold In

Impedance is 100 K $\Omega$ . A TTL low or switch closure at this input causes the generator to stop at the current output level and remain there until released by a TTL high or switch opening.

#### Return In

Impedance is 100 K $\Omega$ . A TTL low or switch closure at this input causes the output level to ramp back to the start value. The ramp rate is front panel selectable from 0 to 100 ms per point.

#### TRIGGER SOURCES

#### Manual

Use the Trigger pushbutton switch on front canel to operate internal trigger circuitry. The slope polarity can be set via the display menus.

External

Use the communication ports (GPIB or RS-232-C) or the Trig In connector on front panel. Trig In connector frequency input can be up to 1 MHz. The slope polarity can be set via the display menus.

#### WAVEFORM CHARACTICS

Horizontal Resolution Up to 8192 points. Vertical Resolution 4095 bits ( - 2047 to + 2047). Rise/Fell Time

<350 ns.

## COMMUNICATION PORTS (OPTIONAL)

#### IEEE-488 Port (Option 001)

Type: IEEE-488-1978 compatible, nonisolated, double buffered. Address: 0-30, internal DIP switch selectable or front panel selectable. Subsets: SH1, AH1, T6, TE0, L4, SR1, RL1, PP0, DC1, C0, E1.

## RS-232-C Serial Port (Option 002)

**Communication:** Full duplex (bidirectional) with CTS/DTR or XON/ XOFF handshaking.

Connector: Rear panel mounted DB-25 (female) with DCE or DTE configuration. Data Format: 8 bits, no parity, one stop bit.

**Data Rate:** 14 steps internal switch selectable (50, 75, 110, 134.5, 150, 200, 300, 600, 1200, 1800, 2400, 4800, 9600, 19,200).

# GENERAL

#### Environmental

**Temperature Range:**  $+23^{\circ}C \pm 5^{\circ}C$ for specified operation, operates 0 to  $+50^{\circ}C$ , -20 to  $+75^{\circ}C$  for storage. **Warmup Time:** 20 minutes for specified (guaranteed for 1 year) operation.

Vibration: 5 to 55 Hz with maximum of 2g at 55 Hz.

Shock: 30g, 11 ms half sine.

Altitude: Sea level to 10,000 ft. for operation. Sea level to 40,000 ft. for storage.

Relative Humidity: 95% at 25°C and at sea level (non-condensing).

Dimensions: 21 cm (8.27 in ) wide. 10 cm (3.94 in.) high, 32.3 cm (12.72 in.) deep.

Weight: 3.55 kg (7.8 lb) net, 4.68 kg (10.3 lb) shipping.

Power: 90 to 128, 180 to 256 rms: 48 to 66 Hz; single phase: <25 VA.

#### OPTIONS

ÚÚ1: IEEE-488 (GPIB) Port For instrument control or entering waveform data.

002: RS-232-C Serial Port

For instrument control or entering waveform data.

NOTE. Options 001 and 002 are mutually exclusive.

# Data Translation DT2801-A Multifunction Input/Output Board

Analog Input Specifications: Accuracy Resolution

Programmable gain Accuracy

Noise Linearity Gain error Offset error Temperature Operating Range Monotonicity A/D zero drift

Amplifier zero drift

Gain drift

Dynamic performance Throughput

Input Specifications Number of channels

Maximum input voltage without damage, power on

Input noise Channel to channel input error Coding

#### Ranges

Programmable input ranges bipolar unipolar

#### DT2801

12 bits: DT2801. DT2801-A 16 bits: DT2801/5716 1. 2. 4. 8 =0.03% FSR (gain=1): 12-bit A/D =0.05% FSR (gain=2.4.8): 12-bit A/D =0.0075% FSR (gain=1): 16-bit A/D ±0.01% FSR (gain=2.4.8): 16-bit A/D

0.03% FSR RMS To within ±½ LSB Adjustable to zero Adjustable to zero

0 to 50°C 0 to 50°C  $\pm 20\mu V/^{\circ}C$  (12-bit A/D)  $\pm 12\mu V/^{\circ}C$  (16-bit A/D) ( $\pm 3\mu V/^{\circ}C$ ) x gain (12-bit A/D) ( $\pm 2\mu V/^{\circ}C$ ) x gain (16-bit A/D)  $\pm 35$ ppm of FSR/°C (12-bit A/D)  $\pm 15$ ppm of FSR/°C (16-bit A/D)

13.700 Hz typical(DT2801)

27.500 Hz typical(DT2801-A) 2.500 Hz typical(DT2801/5716)

16 SE or 8 DI (jumper selectable on 12-bit A/D) 8 DI only (16-bit A/D)

 $\pm 30V (12$ -bit A/D)  $\pm 16V (16$ -bit A/D)  $10\mu V RMS$  $\pm 10\mu V$ Straight binary. offset binary (12-bit A/D) Two's complement. bipolar (16-bit A/D)

±1.25V, 2.5V, 5V, 10V 0 to +1.25V, 0 to +2.5V, 0 to +5V, 0 to +10V

# Analog Output Specifications: DT2801, DT2605 and DT2818

Accuracy	
Resolution	12 bits
Non-linearity	0.02%
Differential linearity	±14LSB
Dynamic Performance	
Settling time to 0.01%	35µS
FSR (10V step)	
Settling time to 0.01%	10µS
FSR (100mV step)	
Slew rate	$0.50V \ \mu S$
Temperature	
Operating Range	ი to +50°C
Monotonicity	0 to +50°C
Offset drift (unipolar)	
Offset drift (bipolar)	±30 ppm of FSR/°C
Gain drift	±30 ppm of FSR/°C
Output Characteristics	
Range	$\pm 10V. \pm 5V. \pm 2.5V.$
	0 to +10V. 0 to +5V
	liumper selectable)
Number of channels	2
Data Coding	Binary, offset binary
Current Output	5mA maximum
Impedance (de)	<0.10
Noiseirms	<0.05% FSR
Capacitive loading	0.5 <i>u</i> F
Protection	Short circuit protected
Throughput to memory	14.8kHz/channel, single channel mode (DT2801)
<b>G</b> ( <b>F F F F F F F F F F</b>	8kHz/channel, dual channel mode (DT2801)
	29.5kHz/channel, single channel mode (DT2801-A)
	16 5kHz/channel dual channel mode (DT2801-A)

# Digital I/O Specifications: DT2801, DT2805, DT2808, DT2818

Digital Input Specifications Logic load	Presents 1 LSTTL load
Digital Output Specifications	
Fanout	Drives 37.5 LSTTE loads
High-level output voltage	2.0V minimum
Low-level output voltage	0.5V maximum
High-level output current	-15mA maximum
Low-level output current	24mA minimum
External Trigger Specifications	
Logic load	Presents 1 LSTTL load
Input type	Schmitt Trigger-edge sensitive
Minimum pulse width	200ns
External Clock Specifications	
Logic load	Presents 1 LSTTL load
Input type	Schmitt Trigger-edge sensitive
Minimum pulse width	200ns
Physical/Environmental Specifications:	DT2801, DT2805, DT2806, DT2808, DT2818
Dimensions	4.5" H X 13.5" W X 1" D
(including connector)	(11.4 X 34.3 X 2.5 cm)
Operating Temperature Range	0 to 50°C
Storage Temperature Range	-25 to 70°C
Humidity	90% non-condensing
Power Consumption	+5V • 1.2A typical



#### INDUSTRIAL DRIVES Lad ond, Virginia

2106 SERIES

ĊŌ.	257	15	155	UE	4	
WRIT	TEN	RE(+ 4-06	API	ROVE	DVLL	49966
SHE	ST	1	OF	_		_

BRUSHLESS SERVO MOTOR .

MOTOR PA		WINDING DATA						
		Tal	Symool	Units	A	В	C	
Horsegower		Adad	Ho fits	HP I	3.8	6.0	10.0	
Scent		Asteo		лры	3350	5250	7500	
				15 • ft	6.0	6.0	7.0	
lorgue		- Dealth	TPag	N•m	7 7.8	1.6	9.1	
	_	Rated	IRid	aince AMS	5.2	8.2	16.6	
Volta (kne to kne)		Rolled	V Rtd	Volts RMS	210	210	210	
Continuous Torque (Stall)		1		115 + 11	10.3	10.4	10.2	
3 40° C Ambient		Nom.	TC	N + m	14.0	14.0	13 9	
Cont. Line Current	_	NOTL	IC	arnos FMS	9.1	14.2	24.4	
Stor Terms		1. 110-0				- 40 E.	1 - 2 (4)	
Hele I Crow		regen.	10		29	29.3		╺╍╴╼┽╼╼╸╼╼
Peak Line Current		I NOR.			12	53	199	
Theoretical Assessments		Nom.	Q m	red/sec	45500	46250	50000	
							المراجعين المحمد	
				IS . IVAMB HMS	1.14	0.73	0.42	
Torque Sensitivity	-	1 1 10%	110		1.55	0.99	0.56	
Back EMF (line-te-line)		1 = 10%	1 KB	IV/XEPM	92.5	59.9	34.4	
No Load Goersane Sceed	_	i Nom.		RPM	4150	6550	17500	
Max Line to Line Volta		Mex	V Mes	Volta AMS	250	250	250	
OG Ass @ 29C (Interiorial		± 10%	RM	Ohms	1.92	0.77	0.26	
		2 30%		Intri	18	7.3	2.4	
Time Constant	Mecn	Nom	I TM	manc	1.0	1.0	11.0	
3 29 C	liec	Nom	TE	Deam	10.9	11.2	10.3	
Marine Commence Champer								
water Operating Characte	البلك وعالوه					1	<u>   </u>	

i

Motor Cycle Curve for Internation Operation Motor Temperature Alse Curve System Penormance Curve

1

-----

PCī 1 ī T PC-25708 25709 25710 Ī

	15	Ymooi		i Value
	}		10 . TE . SOC	10.000639
fotor inemis		JM		0.000866
Weight		wi		
Static Friction		TE		0.07
Thermai Time Constant	1	TCT	iminutes	156
VISCOUL CEMDING	1		ID + IVKRPN	10.0248
# Z Source	!	Fl	IN THE KEIP	10.033
E ECN - DATE	APPO	ISSI	ECN -	DATE APP D
. ADD PC -14 8/21	/84	11	i	
. 74299 . 3/8/	85	1. 1.		
. 74693 1 3,12	,186	<u>. 1</u>	;	· ·
	1	1 1	1	

i



Materia

ī

. RPM

7500





Penny+Giles

- Almost limitless life
- No electrical sliding contacts
- Infinite resolution
- Free from micro-linearity errors
- d.c supply, d.c output
- Low operating torque
- 0-10, 0-20 or 4-20mA output versions available.

The Penny & Giles d.c/d.c angular position sensor is basically a transformer in which the output is governed by the angular position of the input shaft in relation to the transducer body. The output is electrically isolated from the input. The required input is a stabilised 10V d.c. from a source impedance of less than 1 ohm. The d.c. input is converted to an a.c. waveform by an integral oscillator and then fed to the transformer primary winding. The output from the secondary winding is converted to d.c. by an integral demodulator and filter.



#### Specification

(

Model	3810/300	3810/200	3810/100	3810/60	3810/30	3810/20	3810/4	
Effective electrical angle degrees	300	200	100	60	30	20	4	
Output sensitivity per degree - nominal	33mV	50mV	90mV	140mV	240mV	340mV	470mV	
Residual voltage – maximum at 0° arc	50mV	50mV	500mV	1.0V	1.4V	1.6V	3.6V	
Linearity – deviation from best straight line	±0.5%							
Resolution	infinite							
Output ripple (> 1.2k Hz)	0.05% FS	+ 0.4% outp	ut					
Input current nominal	50mA at 10	0.00V d.c.						
Mean temperature coefficient	+10°C to +40°C ±0.8mV/°C			-20°C to	+60°C ±2m	nV/ºC		
Frequency response (PHASE ?)	at 40Hz output 1% down			at 80Hz output 10% down				
Temperature range – optional storage	-20°C to + 60°C -40°C to +100°C							
Mechanical angle	360 degre	es continuou	s					
Torque – maximum	0.5gm cm							
Shaft rotation	clockwise	for increasing	g output					
Options				-				
Current output	Alternative units with 0–10, 0–20 or 4–20mA are available. Please ask for details							
Shaft rotation	anti-clockwise for increasing output							
Sealing	Shaft seal	can be speci	fied (torque i	ncreases wit	h this option)	)		
Absolute linearity	span and zero board available to provide absolute linearity accuracy							

Penny+Giles

#### Penny & Giles Potentiometers Limited

Constant and Challet descel. Co. 1.1. Brief and 11-14

# **Angular Position Transducers**

# Environmental specification

Terminal security and solderability	MIL-R-12934	
Vibration	20G - BS2G100 Grade A extended to 5000Hz	
Acceleration	17G – BS2G100 Grade C Class 1A (i)	
Tropical exposure	BS2G 100 Part 2 Clause 200 (b)	
Temperature and pressure	BS2G 100 Grade A Curves C, D and F	
Radio interference to	BS2G 100 Part 2 Clause 227	
Magnetic interference to	BS2G 100 Part 2 Clause 227	

# **Dimensional specification**



- **Notes** i) The performance specification is true only for a  $10.00V \pm 1 \text{ mV}$  d.c. input with a  $10k\Omega \pm 0.2\%$  load impedance on the output. ii) A stabilised d.c. supply is necessary.
  - iii) There is no short circuit protection across the output.
  - iv) Setting up procedure: align ident groove on the shaft end with the spot on the case, then with a 10.00V d.c. supply and the output fed into a 10kΩ load adjust the shaft with respect to the case until the output corresponds with the index voltage marked on the individual transducer. This will then give precise mid range.

# **Quality Status**

Penny & Giles Potentiometers Limited carries design, manufacture and inspection approvals to Nato standard AQAP 1 Ed. 3 (previously MOD Def. Stan 05-21) and to Civil Aviation Authority requirements



Registered in England number 843904 Registered office as above -



Doc. ref. APT October 1986

# SCREW CONFIGURATION FOR W & P ZSK-30







# DIALKYL PEROXIDES

# INTRODUCTION

PRODUC

JLLETIN

Dialkyl peroxides are organic compounds that have the following general formula:

R'—\_\_\_(OOR)<sub>x</sub> where R' and R are alkyl or substituted alkyl groups

Di-tertiary alkyl peroxides are among the most stable of all the commercially available organic peroxides.

For the most common monofunctional di-tertiary alkyl peroxides;

 $R = R' = \underline{t}$ -alkyl or  $\underline{t}$ -aralkyl

such as Luperox 500,



X = 1, R = R' = t-aralkyl

For the most common difunctional di-tertiary alkyl peroxides;

X = 2

R = <u>t</u>-butyl

R' = t-alkyl diradical

such as Lupersol 101,



The free radicals generated from dialkyl peroxide decomposition are efficient for **crosslinking** polyolefins (polyethylene and ethylene-vinyl acetate); **vulcanizing agents** for elastomers (ethylene propylene copolymers and terpolymers); **curing agents** for polyester resins; **initiators** in bulk, and suspension vinyl polymerizations and as **synergists** for flame retardant polymers.

# **COMMERCIAL DIALKYL PEROXIDES**

Typical physical and chemical properties of commercially available di-tertiary alkyl peroxides are enclosed. For greater convenience in handling and storage, some are available on an inert filler.

# REACTIONS OF DIALKYL PEROXIDES Primary Reaction

When subjected to heat or irradiation, dialkyl peroxides decompose homolytically into two free radicals;

# Secondary Reaction

Tertiary alkoxy radicals can undergo further fragmentation (e.g. B-scission) to form ketones and alkyl radicals;



Radicals produced by either primary or secondary reactions initiate the desired free radical reaction.

## Acid or Base Hydrolysis-Ionic Decomposition

In the presence of strong bases, di-tertiary alkyl peroxides are unattacked.

In the presence of strong oxidizing agents, reducing agents and accelerators (cobalt naphthenate or dimethylaniline) di-tertiary alkyl peroxides can decompose ionically forming non-radical products. Such products do not initate free radical reactions.

Decomposition

# Decomposition Products

The decomposition kinetics of dialkyl peroxides in dilute benzene solutions are first order. Similar behavior has been observed in a polymer matrix.<sup>1</sup> In both cases, the rate determining step appears to be the homolytic cleavage of the oxygen-oxygen bond (primary reaction).

The chemical nature of the radicals depend upon their environment. For example:

In the presence of ABSTRACTABLE HYDROGENS on a polymer they can abstract hydrogen forming new polymer radicals which can then combine to form a crosslink bond.

In the presence of other reactive species in a polymer, such as DOUBLE BONDS, the radicals can also react via addition-type reaction forming different polymer radicals, which can combine or react with additional such polymers to form multiple cross-link bonds.

(1) G.A. Harpell & D.H. Walrod, Rubber Chem. & Tech., Vol. 48 No. 4 Sept. 1973, "Organic Peroxides for Cure of Ethylene-Propylene Rubbers."



In a gas phase or in an inert media, the radicals will decompose forming ketones, alkanes and alkenes. e.g.:

Typical decomposition products of dialkyl peroxides in inert medias are included in the physical characteristics section for each peroxide.

# STORAGE AND HANDLING

#### **Facilities**

Dialkyl peroxides should be stored in a cool-(<100°F) place, separated from the manufacturing area, away from other combustible materials, and in accordance with the labeling designed for each specific package. Storage buildings should be well ventilated.

#### Storage Temperatures

To minimize evaporation and loss of active oxygen, dialkyl peroxides should be stored below 100°F.

# HANDLING PRECAUTIONS

#### **Containers (other than Liqua-Bins)**

Dialkyl peroxides should be stored in their original container. Drain containers completely and flush with a suitable solvent, such as odorless mineral spirits, before discarding. Render the containers non-usable. Never allow residual peroxide to remain undiluted in discarded containers.

# LIQUA-BIN CONTAINERS

This 3500 pound (net), 450 gallon container is a stainless steel package designed for repeated use. Specific handling and use information is available upon request. (Liqua-Bin containers used for Luperox 500T and Luperox 500R product packaging only.)

Materials of Construction — Materials of construction in contact with dialkyl peroxides should generally be limited to inert materials like polyethylene, Teflon, Nylon and Kel-F, reinforced plastics, Type 304 and 316 stainless steel or Tantalum.

**Fiammability** — Di-t-butyl peroxide has a low flow point and its vapors are highly flammable, thus it must be handled as a Flammable Liquid. All other dialkyl peroxides have relatively high flash points, but once ignited, burn vigorously and are very difficult to extinguish. All dialkyl peroxides should be kept away from sources of heat and ignition such as radiators, steam pipes, direct rays of the sun, sparks and open flames.

Contamination — Care should be taken to avoid all forms of contamination with peroxides, particularly oxidizing and reducing agents and metal salts - "Especially strong mineral acids."

Static Electricity — When handling dialkyl peroxides, generally accepted methods of reducing static electricity, e.g.: grounding of equipment, shortening freefall of material, etc. are recommended.

#### FIRE

If a small fire occurs, class B type extinguishers (dry chemical foam or carbon dioxide) can be used. In case of a fire involving large quantities of dialkyl peroxides, the area should be evacuated and the fire fought with water spray or foam.

# SPILLAGE AND DISPOSAL

Small Quantities — If a small quantity of a dialkyl peroxide is spilled, an inert absorbent material, such as vermiculite, should be used to soak up (liquids) or dilute the solid peroxide. The sweepings can then be disposed of by burning in a remote area.

Large Quantities — Larger quantities of dialkyl peroxides should be diluted to less than 1% active oxygen or less than 10% assay, whichever is lower with kerosene or Fuel Oil #2 and subsequently burned in a suitable furnace or incinerator. Provisions must be made for introducing the dilute peroxide solution into the furnace or incinerator as slowly as practicable. Dialkyl peroxides burned under these conditions will emit less air pollutants into the atmosphere since the peroxide is destroyed completely and effectively.

The above procedures should not be employed if in violation of Federal, State or Local regulations.

# TOXICITY

All the physiological effects have not been determined for dialkyl peroxides. In general, dialkyl peroxides should be considered mild skin and eye irritants. The following data has been reported:

Maste.

Dialkyi Peroxide	Eye Irritation	Skin Irritation	Acute Oral Toxicity LD <sub>50</sub> in Rats	genicity Ames Test	
Di-t-butyl peroxide	slight	slight	>25,000 mg/kg	Negative	_
Luperox 500	slight	mild	4100 mg/kg	Negative	
Lupersol 101	slight	slight	3200 mg/kg		
Lupersol 130	slight	slight	1850 mg/kg*		
Lupersol 801	slight	severe	5.18 ml/kg**	Negative	

\*Value listed represents acute intraperitoneal toxicity LD<sub>50</sub> in mice. \*\*( ~4895 mg/kg)

#### **FIRST AID**

Care should be exercised by all personnel handling dialkyl peroxides. Do not allow prolonged contact with skin. Inhalation of vapors or decomposition products emitted during processing should be avoided.

In case of skin or eye contact with a dialkyl peroxide or its decomposition products, wash skin with plenty of soap and water, immediately flush eyes with water for at least 15 minutes and get medical attention. If swallowed, do not induce vomiting, call a physician.

(Continued on back cover.)



				i.					
			· · ·		, T	st Rate iant	ctivation N L MOL	ite C	Hart-ute C
Trade Name	、 General Name	f Formula	Concentration	Temp	1': H	K Fir Order Const	ΔE Α Energ ιKCA	1 Hr Hailit Temp	t, t. Temp
A. Luperox 500R	Dicumyl Peroxide	Сн, сн, Сн, сн, Сн, сн,	0.2M (Benzene)	130 145	1.8 0.28	0.377 2.47	38	136	116
B. Lupersol 101	2,5-Dimethyl-2,5-di (t-butylperoxy) hexane	CH3 (CH3)3COO-C-CH2- CH3 2	0.1M (Benzene)	115 130 145	17 2.3 0.40	0.042 0.247 1.71	40	138	119
C. Lupersol 801	t-Butyl Cumyl Peroxide	CH3 (CH3)_C-00-CC CH3	0.2M (Benzene)	115	17.2	0.040	36	142	121
D. Lupersol 130	2,5-Dimethyl-2,5-di (t-butylperoxy) hexyne-3	CH3 (CH3)3COO-C-C≡ CH3 _ 3	0.1M (Benzene)	115 130 145 160	49 8.2 1.7 0.31	0.014 0.084 0.410 2.22	38	149	126
E. Di-t-Butyl Peroxide	Di-t-Butyl Peroxide	(CH3) <sub>3</sub> C-O-O-C (CH3) <sub>3</sub>	0.2M (Benzene)	100 115 130	220 34 6.4	0.003 0.020 0.018	36	149	126

NOTE: Half life values in polymers may differ.



1740 Military Road / P.O. Box 1048 / Buffalo, New York 14240 / (716) 877-1740 / (800) 558-5575

#### MATERIAL SAFETY DATA SHEET

Folling IL LUGE: 000
----------------------

MATERIAL

A SHEE

Revision Date: 02/09/89 Supersedes Form Dated: 12/22/88

TRADENAME	LUPERSOL 101
CHEMICAL NAME	2.5-dimethy1-2.5
	(t-buty]peroxy)hexane
MOLECULAR FORMULA	C <sub>16</sub> H <sub>34</sub> O <sub>4</sub>

8ġ

.

CHEMICAL	FAMILY		Organic	Peroxide
SYNONYMS	but and in	1.1.4.4-	tetramet	-4, [-1,4
C.A.S. RE	EGISTRY NUMBER(S	)	llaimetr	78-63-7

	HAZ	ARDOUS INGR	EDIENTS			
	Materials or Components		<u>% w/w</u>	Hazard Data		
	<b>2,5-dimethy</b> l-2,5-di(t-butylperoxy)hexa	ne	91-93			
	di-t-butyl peroxide 3,3,6,6-tetramethyl-1,2-dioxacyclohexa 2,2,5,5-tetramethyltetrahydrofuran	ane	2-4 4-6 0.1 - 0.3	•" • <sup>*</sup>		
-	SHIPPING INFORMATION					
	D.O.T. SHIPPING NAME	,5-Di- nexane roxide	I.D. NUMBER FREIGHT CLASSII IMDG CODE PAGE	UN2155 FICATION Chemicals NOIBN 5173		
•••	. PHYSICAL PROPERTIES					
1	MELTING/FREEZING POINT, °C MOLECULAR WEIGHT SPECIFIC GRAVITY (H <sub>2</sub> 0 = 1), 25/25°C S.A.D.T. 30 Pound cont	8 290 0.865 86°C, tainer	VAPOR PRESSURE VAPOR DENSITY % VOLATILES BY APPEARANCE & OI SOLUBILITY in I	(mm Hg)10 @ 115°C (Air = 1)10 VOLUME		
••	FIR	E AND EXPLOS	ION DATA			
•	FLASH POINT, °C/°F. EXTINGUISHING MEDIA. SPECIAL FIRE FIGHTING PROCEDURES UNUSUAL FIRE & EXPLOSION HAZARDS	43/110 Water Fog, If large am safe distan Contaminati fined durin	Dry Chemical, F lount is involve loce. Cool surro on, Temperature lg exposure to f	oam d, evacuate area and fight fire fro unding material with water. - Can decompose with force if con- ire.		
		REACTIVITY	DATA			
	STABILITY CONDITIONS CONTRIBUTING TO INSTABILITY INCC#PATIBILITY (avoid contact with) HAZARDOUS DECOMPOSITION PRODUCTS	Unstable Exposure to Strong acid Decompositi Methane, et t-amyl alco	heat, contamin ls, strong oxidi on products are chane, ethylene, bhol	ation zers flammable and can self-ignite. acetone, t-butyl alcohol and		
	CONDITIONS TO AVOID	Heat, flame Rapid decom	es, sparks, igni position may oc	tion sources, contamination cur at temperatures above 76°C		
,	SP	SPILL OR LEAK				
	STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED	Absorb with sparking to Consult with number of y	Vermiculite/Pe bols and dispose th a Lucidol rep your state's haz	rlite, sweep or scoop up using non- of immediately resentative for the telephone ardous waste agency.		

#### MATERIAL SAFETY SHEET

Page 2

:4 - .

TOXICIT	Y 	
LD <sub>50</sub> = 32000 mg/kg LD <sub>50</sub> = 4.1 ± 1.3 gm/ LC <sub>50</sub> = N/E LD <sub>50</sub> = 1700 mg/kg	kg	
,		
HEALTH HAZARD I	NFORMATION	
	82009422722788888888442084429733	
EYE - Mild (transient)	CORROSIVITY	SKIN - N/E EYE - N/E N/F
N/E	OTHER	N/E
Do <u>NOT</u> induce vomiting. Ge Flush with soap and water.	t emergency medical attention for Contaminated clothing - remove &	lavage. launder. Get medical
IMMEDIATELY flush with plen	ty of water for at least 15 minut	es. Get medical
Remove to fresh air. If no attention.	t breathing, give artificial resp	iration. Get medical
SPECIAL PROTECTION	INFORMATION	
Use with adequate ventilati Safety glasses, goggles Neoprene, natural rubber Can or cartridge gas or vap Eyewash station	on. Local exhaust. Hor	
ipment		
LABEL PRECA	UT IONS	
Wash thoroughly after handl Do not get in eyes, on skir Do not store near combustit Empty container may contair Keep container closed Keep away from heat, sparks Use explosion proof equipme	ing or clothing les hazardous residues , and flames ent	
Do not reuse container . Store below 100°F (38°C) to	o maintain active oxygen content	
ADDRESS: 1740 Military Road	. Buffalo, NY 14240	PHONE: (716)877-1740
	TOXICIT TOX	TOXICITY TOXICITY TOXICITY TOXICITY TOXICITY TOXICITY TOSO = 4.1 ± 1.3 gm/kg TCSO = W/E TCSO = W/E TCSO = W/E TCSO = 1700 mg/kg TCSO = 1700 mg/kg TCSO = 1700 mg/kg TCSO = 0.000 mg/kg TCSO = 0.0000 mg/kg TCSO = 0.00000 mg/kg TCSO = 0.0000 mg/kg TCSO = 0.00000 mg/kg TCSO = 0.0000 mg/kg TCSO = 0.0000 mg/kg TCSO =

NOTES: N/E = Not Established N/A = Not Applicable

LUPERSOL 101

The above information is accurate to the best of our knowledge. However, since data, safety standards, and government regulations are subject to change and the conditions of handling and use, or misuse are beyond our control, Pennwalt MAKES NO WARRANTY, EITHER EXPRESS OR IMPLIED, WITH RESPECT TO THE COMPLETENESS OR CONTINUING ACCURACY OF THE INFORMATION CONTAINED HEREIN AND DISCLAIMS ALL LIABILITY FOR RELIANCE THEREON. User should satisfy himself that he has all current data relevant to his particular use."

UNABLE TO FILM MATERIAL ACCOMPANYING THIS THESIS ( I.E. DISKETTE(S), SLIDES, MICROFICHE, ETC...).

PLEASE CONTACT THE UNIVERSITY LIBRARY.

INCAPABLE DE MICROFILMER LE MATERIEL QUI ACCOMPAGNE CETTE THESE (EX. DISQUETTES, DIAPOSITIVES, MICROFICHE (S), ETC...).

VEUILLEZ CONTACTER LA BIBLIOTHEQUE DE L'UNIVERSITE.

NATIONAL LIBRARY OF CANADABIBLIOTHEQUE NATIONALE DU CANADACANADIAN THESES SERVICELE SERVICE DES THESES CANADIENNES

Appendix E: Manuals for BASIC Communications Programs, MACO 8000 Interface